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May 7, 2002

Mr. Tien Q. Duong
5G-030, EE-32
Forrestal Building
U.S. Department of Energy
Washington D.C. 20585

Dear Tien:

Here is the second-quarter FY 2002 report for the Batteries for Advanced Transportation Technologies (BATT) Program. This report and prior (ETR) Program reports can be downloaded from http://berc.lbl.gov/BATT/BATT.html.

Sincerely,

Frank McLarnon

Frank McLarnon
Manager
BATT Program

cc:	R. Sutula	DOE/OAAT
	R. Kirk	DOE/OAAT
	V. Battaglia	ANL
	K. Abbott	DOE-Oakland

LBID-2411

BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT) PROGRAM

QUARTERLY REPORT

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Task Status and Progress Toward Milestones Reports by Research Area

BATT TASK 1
CELL DEVELOPMENT

TASK STATUS REPORT

PI, INSTITUTION: K. Striebel, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Development - Cell Fabrication and Testing

SYSTEMS: Low-Cost Li-Ion, High-Power Li-Ion

BARRIER: Inconsistent evaluation of the merits of candidate novel materials.

OBJECTIVES: The primary objective is to benchmark the performance of new materials for low-cost and high-power Li-ion cells.

APPROACH: The testing of novel materials in a standard cell with preset protocols will provide the necessary link between the invention of novel battery components and the diagnostic evaluation of failure modes, and will accelerate the development of a battery-powered EV. Novel components will be developed in BATT Program Tasks 2, 3, and 4 (anodes, electrolytes, and cathodes) for baseline liquid and gel electrolyte chemistries. These components are incorporated into a standardized cell, tested with a consistent protocol to determine capacity, energy, power, and lifetime characteristics. Components are then delivered to the PIs involved with BATT Program diagnostics. Fabrication and testing of the third baseline cell, namely Li metal/polymer/V_6O_{13}, will be carried out in BATT Program Task 3.1.

STATUS OCT. 1, 2001:

- Cell fabrication and testing equipment, procedures, and protocols are in place for studies of 12 cm^2 laminated-foil pouch cells at various temperatures and constant-current cycling studies.
- Gen 2 chemistry pouch cells with both Quallion and LBNL-made cathodes were cycled 160 times with <5% capacity fade, providing verification of the pouch cell process.
- The high-power baseline cell chemistry has been benchmarked in constant-current testing. Cells have been received from Hydro-Québec for the benchmarking of the high-energy baseline cell against current USABC goals.

EXPECTED STATUS SEPT. 30, 2002: The effort on the low-cost Li-ion baseline cell will be focused on $LiFePO_4$ cathodes, various gel electrolyte components applied to Celgard, and the evaluation of the available natural graphites. Electrode compositions will be optimized for electronic and ionic conductivity with the aid of collaborative modeling studies. Studies of cell and component performance as functions of temperature and electrolyte composition will be completed. Evaluation of new materials for the baseline cells will be underway: $Li_{0.44}MnO_2$ (LBNL), $LiMn_{2-y}Al_yO_{4-z}S_z$ (LBNL), intermetallic anodes (ANL), and layered Mn-based cathodes (ANL).

RELEVANT USABC GOALS: 10 year life, <20% capacity fade over a 10-year period.

MILESTONE: (a) Evaluate cycle-life and power capability of the $LiFePO_4$/gel with $LiBF_4$/natural graphite cell (December 2001). (b) Compare the several approaches to gel-electrolyte cell assembly using standard Li-ion electrodes (June 2002).

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter:**

Work this quarter has continued to focus on the low-cost baseline cell with a $LiFePO_4$ cathode and a natural graphite anode. Cells with various types of gel electrolyte have been received for testing from Hydro Québec. Cells with liquid electrolyte and Celgard separator have been assembled from LBNL- and HQ-prepared anodes and cathodes and tested with our standard protocol. The LBNL-anodes were prepared with SL-20 carbon from Superior Graphite and all of the $LiFePO_4$ cathodes tested contain the carbon-coated material from the University of Montreal. For this material, a high of 148 mAh/g was measured at a rate of C/25 with a HQ-prepared cathode (including a carbon-coated Al current collector) assembled in a Swagelok cell with liquid electrolyte and Li metal.

The early cells received from HQ suffered from leakage problems, high first-cycle irreversible capacity on the anode, and gel instability problems. The fourth (and best) batch of cells is currently under test. Preliminary results with full cells showed a specific capacity of 0.42 mAh/cm^2 and an energy of 1.3 mWh/cm^2 at a C/3 rate. This energy can be compared with 4.3 and 10.8 mWh/cm^2 at C/3 for cells with Co-containing cathodes and synthetic graphite anodes of high-power and high-energy design, respectively. The low energy is due in part to low loading on the cathode (5 mg/cm^2) and the high first-cycle irreversible capacity of the anode. The HQ natural graphite/Li cell with the gel electrolyte showed capacity of 286 mAh/g with about 24% capacity loss on the first cycle.

Seventeen 12-cm^2 pouch cells have been assembled with full cell configuration: $LiFePO_4$/Celgard-1M $LiBF_4$ (EC:DMC)/ natural graphite. The effects of the anode/cathode capacity ratio, charging protocol, electrolyte composition and cathode thickness on cell performance are being studied. These cells showed high first-cycle irreversible capacity loss (ICL) at 20-35% and ICL at second cycle was still 5-10%. Swagelok cell studies on the individual electrodes with a Li CE and Li RE suggests that most of the ICL in full cells arises from the graphite electrode, because the ICL of $LiFePO_4$ in a Swagelok cell was less than 3%. Pressed cathodes deliver better high-rate performance than un-pressed cathodes. This is probably due to improved electronic conductivity of the cathode matrix. The conductivity of these electrodes is being measured at the University of Michigan. The effect of cathode pressing on capacity fade will be reported next quarter.

The capacities of pouch cells with HQ-made electrodes at C/5 and 5C rates were 80 and 50% of the capacity at the C/25 rate, respectively. Our best delivered energy for this cell chemistry with a liquid electrolyte so far was 2.35 mWh/cm^2 at a rate of C/3. This is up from the 1.32 mWh/cm^2 reported last quarter. However, capacity fade of these cells during cycling is still high. Various cells will be delivered to the diagnostics tasks to help understand the dominant capacity fade mechanisms.

A suitable set of conditions (polymer concentration, time and temperature) for the *in situ* cross-linking of gel samples from Daiso (Japan) has been identified with conductivity measurements in blocking-electrode Swagelok cells. Next quarter, pouch cells will be assembled with this gel polymer electrolyte and the well-characterized $LiCoO_2$ and synthetic graphite electrodes from Quallion Corp.

TASK STATUS REPORT

PI, INSTITUTION: T.J. Richardson, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Development - Materials Characterization, Overcharge Protection, Cathode Development

SYSTEMS: Li/Polymer, Low-Cost Li-Ion

BARRIER: Short lithium battery lifetimes, inadequate capacity.

OBJECTIVES: Support cell development through structural characterization of active electrode components before, during, and after cycling. Investigate inexpensive, self-actuating overcharge protection mechanisms. Synthesize and evaluate alternative electrode materials.

APPROACH: *Subtask 1.* Address primary causes of capacity and power fading by correlating them with the composition and structure of electrode active materials using x-ray diffraction (XRD), vibrational spectroscopy, and voltammetry. *Subtask 2.* Develop internal overcharge protection mechanism that becomes active when needed and allows continued, undegraded cycling of unaffected cells. *Subtask 3.* Develop improved cathode materials *via* a rational approach to active material synthesis.

STATUS OCT. 1, 2001: The stability of $LiFePO_4$ at extreme potentials and states of charge has been established. Capacity fading in $LiFePO_4$ due to overcharging has been shown to be due to loss of active material rather than to phase conversion. New phosphate-stabilized cathode materials with high Li content were prepared and characterized.

EXPECTED STATUS SEPT. 30, 2002: Phase transformations and accumulation of decomposition products in cycled electrodes from Task 1.1 will be identified and correlated with cell performance characteristics. The ability of electroactive polymers to provide overcharge protection will be evaluated. Potentially useful new low-cost, high-capacity electrode materials will be synthesized and tested.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Determine phase transformations in cycled cathode materials selected for use in BATT Cell development tasks (April 2002). Determine switching characteristics of electroactive conducting polymer (June 2002). Prepare and characterize novel stabilized Fe and/or Mn cathode materials (August 2002).

PROGRESS TOWARD MILESTONES

Accomplishments toward milestones over last quarter

Subtask 1. Electrodes from cells supplied by Hydro-Québec or made from HQ materials and cycled by LBNL were characterized by XRD and FTIR. The $LiFePO_4$ cathodes from cells LHQ1 and HQ2F were found to be in a nearly fullycharged state by XRD and fully charged by FTIR. The difference is consistent with the relative penetration depths of the analyzing radiation, and supports the “shrinking core” interpretation of $LiFePO_4/FePO_4$ interconversion. Further investigation of this aspect is warranted, as it relates to both capacity and rate performance for this system. The state of charge findings also support capacity fading due to depletion of Li inventory, most likely at the anode-electrolyte interface. The $Li_4Ti_5O_{12}$ anode from HQ2F was found to contain significant amounts of TiO_2 (both anatase and rutile). Analysis of powder from which they were made showed that these phases were present (6 w/o anatase, 7 w/o rutile) in the uncycled electrode. Both electrodes from this leaking cell also contained lithium carbonate, possibly due to hydrolysis of the electrolyte.

Application of FTIR to other cathode systems, including ATD Program Gen 2, appears to be a useful complement to Raman spectroscopy and XRD as it is more bulk-sensitive than Raman and less so than XRD. Standard spectra of electrodes and powders at different states of charge have been collected for comparison with cycled samples.

Subtask 2. Attempts to prepare switching polymer-impregnated separators by chemical and electrochemical polymerization of precursors have thus far failed to produce uniformly distributed polymers. The possibility of using the polymer diode in an alternative configuration, separate from the cell itself is also being pursued.

Subtask 3. Four manganese and iron phosphates with the alluaudite structure have been prepared by solid-state reactions: $Li_{0.75}Na_{0.25}MnFe_2(PO_4)_3$, $Na_2Mn_2Fe(PO_4)_3$, $LiNaMn_2Fe(PO_4)_3$, and $NaFe_3(PO_4)_3$. The latter three are previously unreported phases. $Li_2Mn_2Fe(PO_4)_3$ was prepared from $Na_2Mn_2Fe(PO_4)_3$ by ion exchange. These materials are similar in stoichiometry to $LiFe(Mn)PO_4$, but have a more complex structure that can accommodate mixed transition metal oxidation states. They are of interest because of their somewhat higher electronic conductivity, high intercalant ion mobility, and ease of preparation. An investigation of their electrochemical properties is under way.

A new post-doctoral hire will begin work on this task in June.

TASK STATUS REPORT

PI, INSTITUTION: K. Zaghib, Hydro-Québec Research Institute

TASK TITLE - PROJECT: Cell Development - Research on Lithium-Ion Polymer Batteries Utilizing Low-Cost Materials

SYSTEMS: Low-cost Li-ion

BARRIER: High cost of Li-ion batteries

OBJECTIVES: (a) To fabricate Li-ion polymer cells (4 cm^2 area) using cell chemistries proposed by DOE. Cells (50% of total) will be sent to LBNL for testing. (b) To investigate phenomena at the anode/separator and cathode/separator interfaces. (c) To determine the cycle life of Li-ion polymer cells at different temperatures (55 to 0°C) and self-discharge rates. (d) To synthesize $LiFePO_4$ cathode material for Li-ion polymer cells.
We want to determine the effects of: (1) $LiFePO_4$ particle size, (2) the amount of conductive carbon in the electrodes, (3) the mixed salt concentration (from 1 M to 2 M), on battery performance.

APPROACH: Our approach is to synthesize and prepare electrodes (anode and cathode) with low-cost materials for evaluation in Li-ion polymer cells containing gel polymer electrolytes. The effects of $LiFePO_4$ particle size, the amount of conductive carbon in the electrodes, and the salt concentration (mixed salt, from 1M to 2M) on battery performance will be investigated. The effect of pressure and interfacial phenomena on electrode performance will also be studied.

STATUS OCT. 1, 2001: We completed the coating of electrodes containing graphite, $LiFePO_4$ and $Li_4Ti_5O_{12}$ with variable capacities. Samples of these coated films were sent to LBNL for evaluation. Li-ion gel polymer cells were fabricated and testing was underway.

EXPECTED STATUS SEPT. 30, 2002: Fabricate and send additional cells to LBNL for evaluation. Complete tests to determine the effects of pressure on the performance of Li-ion polymer cells. Select suitable procedure to coat gel polymer as (i) over coating on Celgard separator or (ii) free-standing polymer electrolyte.

RELEVANT USABC GOALS: 10 year life, < 20% capacity fade over a 10-year period.

MILESTONES: Ten cells were provided to LBNL in October 2001 for evaluation. Seven extra cells have been sent to LBNL in December 2001, based on passivation-free chemistry $Li_4Ti_5O_{12}$/gel polymer/$LiFePO_4$. We expect to provide the second deliverable of ten cells by the end of January 2002. We expect to optimize the cell assembly by using a new sealing method.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

We have completed the pressure study on the performance of the polymer gel at the anode and cathodes interfaces by using impedance spectroscopy and scanning electron microscopy. The data show that increasing pressure improves the interfaces and 10 psi is necessary to obtain a good reversible capacity for both electrodes.

Recently, our major effort focussed on studies of the reversible capacity of graphite used in the anode. First we used a new generation of natural graphite and second, we investigated the effect of the porosity of the anode and cathode.After optimization of the porosity, the graphite electrode exhibits better performance. In the first cycle the irreversible capacity was reduced from 50% to less than 25% (Fig. 1).

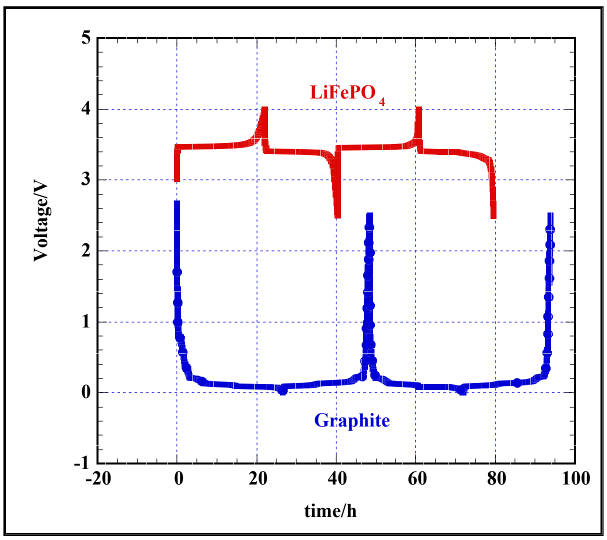


Figure 1

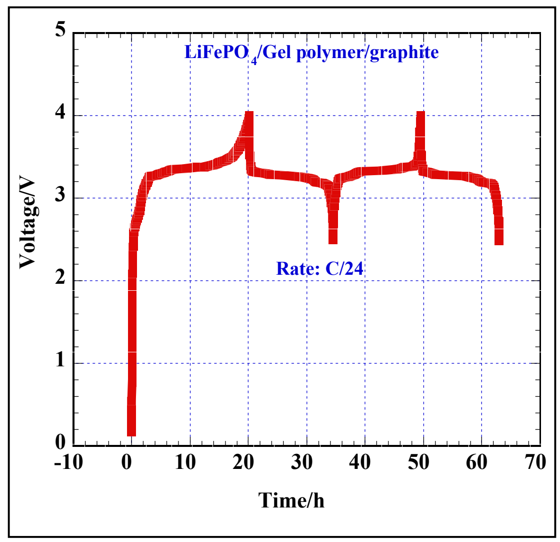


Figure 2

The optimized $LiFePO_4$ and graphite electrodes were evaluated in Li-ion gel cells. The result of the first cycles is shown in Fig.2. The reversible capacity increased by 15% compared to first-generation cells. Ten (10) cells with this cell chemistry were delivered to LBNL in January 2002.

Recently, a second batch of ten (10) cells was sent in March 2002 to LBNL for evaluation. In these cells, we introduced a new polymer electrolyte based on PEO that was coated and electron-beam cross-linked at LTEE(Shawinigan).

- **Further plans to meet or exceed milestones:** We have successfully coated the new gel polymer electrolyte that was cross-linked by electron beam (EB) at LTEE (Shawinigan) facilities. Cells with this new chemistry will be characterized and tested with prolonged cycling.

- **Reason for changes from original milestones:** N/A

BATT TASK 2
ANODES

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Anodes - Non-Carbonaceous Materials

SYSTEMS: Low-cost Li-ion

BARRIER: Cost and safety limitations of Li-ion batteries.

OBJECTIVES: To replace carbon with an alternative inexpensive anode material that will be compatible, in particular, with low-cost manganese oxide cathodes. The project also addresses the need for improved safety of Li-ion cells.

APPROACH: Our approach is to search for, characterize, and develop inexpensive intermetallic electrodes that provide an electrochemical potential a few hundred mV above the potential of metallic Li, and that provide capacities >400 mAh/g and >1000 mAh/ml (the theoretical capacities for graphite are 372 mAh/g and 818 mAh/ml, respectively). The task entails the synthesis and electrochemical evaluation of the intermetallic electrodes and their structural characterization by X-ray diffraction and spectroscopy. The reactivity of the intermetallic electrodes with the electrolyte will be determined by calorimetric techniques.

STATUS OCT. 1, 2001: We identified intermetallic compounds with various structure types that convert to lithiated zinc-blende-type structures during reversible electrochemical reactions. Cu_6Sn_5, InSb, and Cu_2Sb have formed the basis for our studies. Cu_2Sb yielded the best electrochemical performance and stability. Against a Li electrode, Cu_2Sb delivered a stable capacity of ~300 mAh/g, which translates to 1914 mAh/ml, for at least 25 cycles. These novel intermetallic electrodes, which operate by a reversible Li insertion/metal extrusion reaction with an invariant metal host subarray, provided a new approach for the design of alternative anode materials with acceptable capacity, performance, and stability.

EXPECTED STATUS SEPT. 30, 2002: We expect to increase the cycle life of intermetallic electrodes based on tin and antimony to more than 100 cycles with capacities in excess of 300 mAh/g and 2000 mAh/ml in Li half-cells (K. Striebel). Through collaborative efforts, we will have studied the nature of the electrode/electrolyte interface and obtained data on the thermal stability of the intermetallic electrodes with respect to the electrolytes. Detailed structure/electrochemical property relationships will have been obtained primarily by XANES, EXAFS, and XRD studies at the Advanced Photon Source at Argonne and by HRTEM imaging.

RELEVANT USABC GOALS: 10-year life, <20% fade over a 10-year period.

MILESTONES: Our primary milestone will be to achieve a reversible electrochemical capacity of tin and/or antimony based intermetallic electrodes in excess of 300 mAh/g and 2000 mAh/ml for more than 100 cycles by April 2002. Efforts to understand structure/electrochemical property relationships, electrode/electrolyte interfaces, and thermal stability of the intermetallic electrodes will be on going through September 2002.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

We have continued to investigate the possible causes for the irreversible capacity loss in intermetallic electrodes and to obtain "long-term" cycling data for the most promising materials such as Cu_2Sb and iron-doped Cu_6Sn_5. Previous data have shown that despite passivation coatings, particle size effects, electrode porosity and copper diffusion limitations, which can contribute to the irreversible capacity, certain intermetallic electrodes, such as Cu_2Sb, have delivered rechargeable capacities close to 90% of their theoretical value even after the initial charge/discharge cycle. We have therefore directed our research efforts to investigate electrolyte effects as a major cause for capacity loss. Eight different electrolytes, each containing a 1M concentration of $LiPF_6$ salt were investigated. The electrolyte solvents consisted of combinations of ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), propylene carbonate (PC), and γ-butyl lactone (GBL). For these investigations, Li cells with Cu_2Sb and Cu_6Sn_5 electrodes were tested in the voltage range 1.2-0.0 V. Variation in performance was observed for both Li/Cu_2Sb and Li/Cu_6Sn_5 cells, with systems containing EC/DEC and EC/EMC performing the best (as judged by capacity after 20 cycles), while those containing GBL, PC, and high EC concentrations ($50%) performed the worst. Of particular significance, however, was that although the cycling efficiency for both types of electrodes after the initial discharge/charge cycle was high (98-99%), Li/Cu_6Sn_5 cells consistently showed a lower irreversible capacity loss on the initial cycle (~24%) compared to Li/Cu_2Sb cells ($35%).

The long-term cycling of Fe-doped Cu_6Sn_5 cells is shown in Fig. 1. A capacity in excess of 300 mAh/g can be achieved for approximately 30 cycles when the end-voltage of the Li cell is set between 0.1 and 0.0 V. This "high" capacity necessitates the formation of Li_xSn phases during the electrochemical reaction, which contributes to capacity fade. Continued cycling leads to a steady capacity loss, reaching approximately 200 mAh/g after 100 cycles. Greater cycling stability is achieved if the lower voltage is set at 0.2 V when the electrochemical reaction is restricted to a topotactic phase transition that has been described in previous reports and publications. At present, the performance figures fall short of our 2002 target (300 mAh/g for 100 cycles) by approximately 30%.

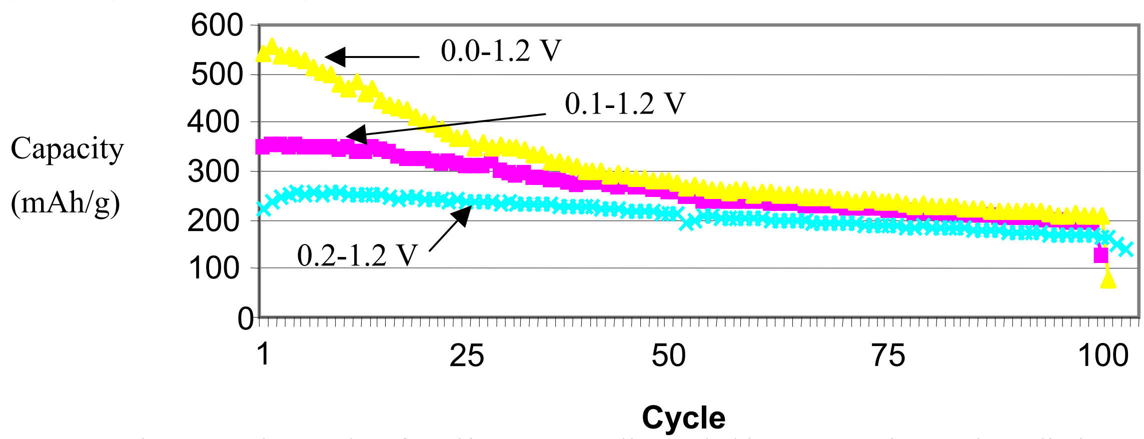


Figure 1. Capacity vs. cycle no. plots for Li/$FeCu_5Sn_5$ cells, cycled between various voltage limits.

- **Further plans to meet or exceed milestones:** Electrolyte studies, which are considered critical for the success of this project, are being continued, as are studies of other Sb- and Sn-based intermetallic electrode materials.

- **Reason for changes from original milestones:** N/A

TASK STATUS REPORT

PI, INSTITUTION: M.S. Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Anodes - Novel Materials

SYSTEMS: Low-cost Li-ion battery and gel battery

BARRIER: Cost, safety and volumetric capacity limitations of Li-ion batteries

OBJECTIVES: To replace the presently used carbon anodes with safer materials that will be compatible with manganese oxide cathodes and the associated electrolyte. In particular we will investigate Mn-tolerant anode materials.

APPROACH: Our anode approach is to explore, synthesize, characterize, and develop inexpensive materials that have a potential about 500 mV above that of pure Li (to minimize the risk of Li plating and thus enhance safety) and have higher volumetric energy densities than carbon. We will place emphasis on simple metal alloys/composites. All materials will be evaluated electrochemically in a variety of cell configurations, and for thermal and kinetic stability.

STATUS OCT. 1, 2001: We determined that vanadium and manganese oxides, in their highest oxidation states, are not prime candidates. Pure Al was found to have a high capacity and it reacted readily with Li, but its capacity faded rapidly upon cycling in carbonate-based electrolytes. Several simple binary alloys of Al showed an even higher capacity fade than Al itself. Tin-containing materials, such as $MnSn_2$ appeared to cycle well for a few cycles, before capacity fade set in.

EXPECTED STATUS SEPT. 30, 2002: We expect to identify several additional non-Al binary alloys, to improve the electrochemical performance of the materials identified, and to design a program to understand and remediate capacity fade upon cycling.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestone is to identify by September 2002 a new simple material (a binary alloy) that has the potential of higher volumetric capacity than carbon at about 0.5 volts relative to pure Li. In addition, we will design a program to identify, understand and mitigate the capacity loss during cycling of simple alloy systems.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

As agreed in the AOP we are now generating a plan to build a better understanding of the capacity loss in simple binary metal systems, particularly for carbonate-based electrolyte systems. One example is $MnSn_2$, which cycles well for a few cycles then decays rapidly. There is a complete reaction (turnover) of the tin of about five before degradation sets in, indicating that the compound is inherently reversible. We will compare this system with the SnBi eutectic, where Sn and Bi are present as separate species and no compound formation occurs upon Li removal.

We are forming Sn_2Mn in a variety of ways, including arc-melting followed either by rolling into a thin-film metallic electrode or powdered and then coated to form an electrode. We will also grow thin alternating films of tin and Mn, collaborating with Professor E. Cotts, then measure their interdiffusion to form tin-manganese compounds and determine electrochemical behavior as a function of film composition and particle size. We will also determine changes in microstructure as the Li is cycled, and the impact of oxygen species on particle stability.

We will compare this system with the Sn-Mo-O system which has been reported to cycle well both as an oxide (Morales *et al*) and as thin metal films (Dahn et al). This system, although possibly too heavy for practical application will act as a promising reference point as in the oxide the Sn and Mo appear to be mutually soluble, in the metal films mixed alloys are present.

The figure below shows the cycling behavior of a rolled metallic sheet of "SnBi", and the x-ray diffraction pattern of the sheet anode before Li insertion and after the first cycle. No major differences are observed, indicating that the SnBi eutectic has reformed with approximately the same particle size. The x-ray diffraction showed the initial formation of Li_3Bi, followed by formation of LiSn, other intermediate phases and finally "Li_4Sn".

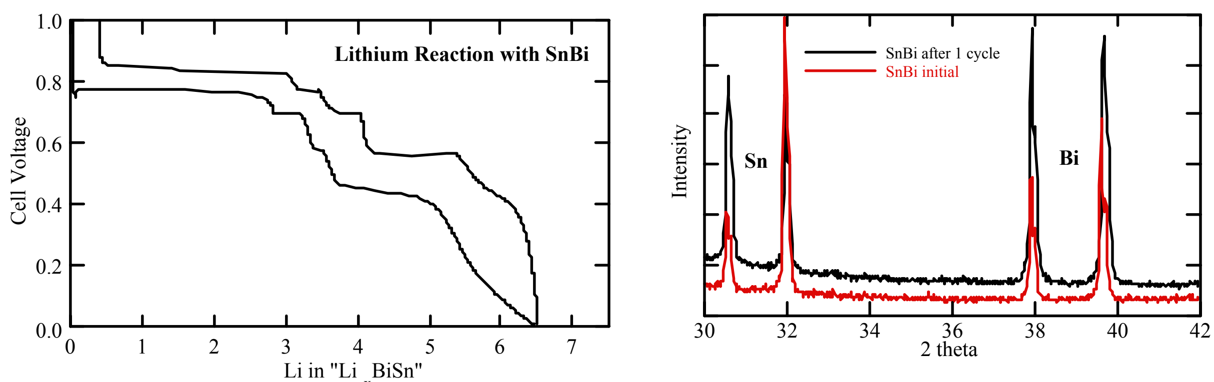


Figure 1. First cycle of insertion of Li into "SnBi" (left), and (right) x-ray diffraction of "SnBi" before initial Li insertion and after Li removal showing that line-widths do not change significantly.

- **Further plans to meet or exceed milestones:** None.

- **Reason for changes from original milestones:** N/A

TASK STATUS REPORT

PI, INSTITUTION: G.A. Nazri and M.D. Curtis, University of Michigan
T. Malinski, Ohio University

TASK TITLE – PROJECT: Anodes - Novel Composite Anode for Lithium-ion Batteries

SYSTEMS: Low–cost Li-ion

BARRIER: Safety, irreversible capacity loss, and self-discharge

OBJECTIVES: The primary objective is to improve the overall safety, cycle life, and shelf life of the Li-ion battery through the development of a novel composite anode with no irreversible capacity loss during initial cycles, and with high energy and power density.

APPROACH: Our approach is to develop composite anode through prelithiation to remove the irreversible capacity loss and provide high performance anode with thermal and chemical stability for application in large size Li batteries. The composite anode will be engineered to be compatible with the existing Li-ion chemistry. The composite anode also provides a new opportunity to construct Li cells using lower cost and stable electrolytes.

STATUS OCT. 1, 2001: We have proposed to develop a composite anode with no irreversible capacity loss and with superior gravimetric and volumetric energy density. Further, this new composite anode will provide a new opportunity to be used in combination with high energy and high rate non-lithiated cathodes that will allow the use of much lower cost electrolytes (PC-based electrolytes). While the focus of our work will be on the development of composite anode, during 2001, we have also developed a Li-phosphonate polymer that is stable in the operational voltage range of carbonaceous anodes with the added benefit of expected fire retardant properties. Also, a unique, *in situ* technique was developed for exploring the reactivity of anode/electrolyte interfaces.

EXPECTED STATUS SEPT. 30, 2002: A novel composite anode with no irreversible capacity loss will be delivered for application in large size Li-ion batteries. The main focus will be on optimization of rate capability, energy density, and safety aspects of the composite anode. The novel process to be developed in this work is applicable to alternative anodes such as carbonaceous anodes, oxides, nitrides, and phosphides systems. Further, the electrode impedance will be minimized for application in high-power batteries.

RELEVANT USABC GOALS: Improved safety of Li-ion batteries, long cycle and shelf life, compatibility for high-power batteries, and new opportunity to develop practical battery for HEVs and EVs.

MILESTONES: Preparation and evaluation of optimized composite anodes with no irreversible capacity loss; 6/15/2002:
We have investigated the possibility of using chemical prelithiation of oxides and nitride anodes. Our preliminary results indicate that our process can transform the oxide anode to metallic state, ready for further formation of reversible Li alloys. Characterization of the composite anode indicates that the anodes consist of nano-clusters of metals stabilized within a lithium oxide matrix (in the case of oxide), and in the lithium nitride (in the case of metal nitride).

PROGRESS TOWARD MILESTONES

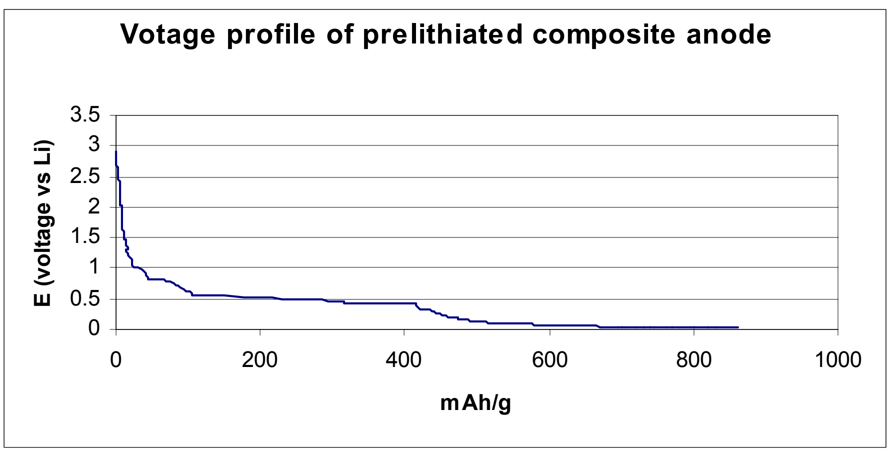
- **Accomplishments toward milestone over last quarter**

Work this quarter has focused on two areas, (a) optimization of pre-lithiated composite anode to control the amount of Li inserted in the anode and (b) the performance of the prelithiated composite anode in Li cells.

(a) we have prelithiated a composite made of natural graphite and tin oxide by a chemical process "mechanomilling technique". Using this process, we have successfully controlled the degree of prelithiation. In the first series of tests, the prelithiation has proceeded only to complete reduction of metal oxide to metallic state. This process was simple and successful. Our x-ray diffraction data, IR spectroscopy, and XPS results indicate complete reduction of oxide to metallic state. In the second series of test, we controlled the prelithiation process to proceed beyond complete reduction of oxide in order to form Li alloys. The process of over-lithiation was also successful. The synthesis has been performed for prelithiation of graphite, SnO, SnO_2, Sb_2O_3, PbO, and CoO. The electrochemical testing of these composites is in progress.

(b) We have examined performances of the prelithiated composite anodes in Li cells. The cell consists of 5 cm^2 metallic Li as counter electrode and Li-Al alloy as a reference electrode. The electrolyte was 0.8M $LiPF_6$ in EC-DMC-PC (50:30:20) in a Celgard separator. The cells were charged and discharged at various current densities ~1 mA/cm^2. Electrode loading was 9.2 mg/cm^2.

Figure shows a typical initial charge of the composite anode indicating no oxide reduction after the pre-lithiation process. Our results clearly show that by using a pre-lithiation process, we can eliminate the large irreversible capacity loss of the composite anodes.



- **Further plans to meet or exceed milestones:**

We are planning to test and evaluate over-lithiated composite anode against cathodes with no Li content, in particular V_6O_{13}. As it is planned, after initial testing, the composite anode will be available to LBNL for further evaluation.

- **Reason for changes from original milestones:** N/A

BATT TASK 3
ELECTROLYTES

TASK STATUS REPORT

PI, INSTITUTION: N. Balsara, J. Kerr, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes - R&D for Advanced Lithium Batteries

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Short Li battery lifetimes, poor ambient-temperature performance for polymer electrolytes, and low energy and power densities due to instability to 4-V.

OBJECTIVES:
- Determine the feasibility of the Li metal electrode with organic electrolytes and provide operating conditions that prevent dendrite growth.
- Determine the limitations on Li-ion transport in polymer electrolytes and composite electrodes and develop new materials capable of ambient-temperature operation with Li metal.
- Determine the limits of stability of organic electrolytes at high-voltage cathode materials (*e.g.*, 4 V) and develop materials and methods to increase stability.

APPROACH: A physical organic chemistry approach is taken to electrolyte design, thereby ensuring that not only are the sources of poor performance and failure pinpointed but also the problem can be corrected through materials design and synthesis.

STATUS OCT. 1, 2001: A study of the effects of polymer electrolyte properties on dendrite growth at Li metal electrodes was completed. Polymer electrolytes were prepared that are designed to define the upper limits of ion transport for polymer electrolytes (conductivity $>10^{-4}$S/cm, $D_s>10^{-8}cm^2s^{-1}$ and $t^0_+>0.3$ at 20°C with LiTFSI). An initial survey of the effect of polymer structure on stability toward high voltage was initiated. Lab cell ($1cm^2$) testing of the Li/polymer system was established and baseline data sets completed.

EXPECTED STATUS SEPT. 30, 2002: Quantitative measurements of the primary factors involved in dendrite growth will be completed (transport and mechanical properties). Transport and mechanical properties will be measured for less costly salts (LiTf, $LiPF_6$ and $LiBF_4$) and the cost *vs.* performance will be assessed. Lithium/polymer and gel-polymer cell testing at an appropriate larger cell size (*e.g.*, 25 or $100cm^2$ area) will be established and compared with Lab cell performance. Diagnostics will be developed to characterize electrolyte/binder changes that cause increase of ASI and capacity fade.

RELEVANT USABC GOALS: 10 year life, <20% capacity fade over a 10-year period, 1000 cycles, operating environment –40 to 65°C, specific energy >170 Wh/kg, specific power >300 W/kg, <150$/kWh @ 20K/year.

MILESTONES:
1. Electrolyte properties that inhibit dendrites measured quantitatively (09/30/02)
2. Complete scale-up for Li/polymer and gel polymer cell construction and testing (12/31/ 02).
3. Establish correlations between large scale and lab cell performance (09/30/02).

PROGRESS TOWARD MILESTONES

1. Accomplishments toward milestone over last quarter: Cycling of symmetrical Li/polymer electrolyte/Li cells and Li/polymer electrolyte/V_6O_{13} cells has been carried on the $1cm^2$ and $4cm^2$ electrode area scale. Electrolytes that have been examined are: PEO-LiTFSI; PEMO-LiTFSI; comb branch polymers $PEPE_3$-LiTFSI and $PEP(TMO)_3$-LiTFSI and linear cross-linkable PEO, polyoxetane and poly(EOTMO) all with LiTFSI. (TMO stands for trimethylene links between the ether oxygens and EO for ethylene links). Some cells have been successfully built with reference electrodes to allow examination of the impedance of the individual electrodes.

Dendrite growth appears to depend upon salt concentration in a complicated fashion that also depends upon the cell configuration. In lithium/PEO-LiTFSI/V_6O_{13} cells dendrites formed rapidly at low salt concentrations whereas dendrites appeared much less quickly at high concentration. This is the opposite trend to that observed for symmetrical Li/Li cells and indicates that care is needed in the interpretation of symmetrical cell data when applying it to full cells. It was also noted that low M.Wt. PEO (200K)-LiTFSI formed dendrites more rapidly than high M.Wt. PEO(5000K), and this M.Wt. variation is consistent with results observed with PEMO (amorphous PEO). The M.Wt. affects the mechanical properties, as does the presence of fillers. Improvements have been observed to the mechanical properties of low M.Wt. PEO due to the addition of filler materials such as fumed silica and alumina. Rheological and thermal measurements have been completed on these filled electrolytes that show no great effect upon the kinetics of crystallization. The effect of filler on the polymers appears to be a free-volume effect. Preparation of cross-linked polymer electrolytes has been carried out and rheological and electrochemical testing is presently under way to provide detailed quantitative measurements of the polymer electrolyte properties.

- **Further plans to meet or exceed milestones:** Modification of the Li surface will be studied to reduce the interfacial impedance. Transport properties for the comb branch EO and TMO polymers will be obtained as a function of cross-link density.

2. Accomplishments toward milestone over last quarter: This milestone is essentially complete. Large batches (100g) of pre-polymer have been prepared and the structures of the cross-linking units have been varied to allow the mechanical properties to be tuned. Bulk rheology measurements have been completed on PEO and PPO samples to verify the measurements. Large-area membranes (12-25cm^2) have been cast to provide freestanding films with varying degrees of cross-linking. Two different cross-linking chemistries are under test – hydrosilation and radical initiation methods. The cross-linked membranes are usable as “dry” polymer electrolytes and as gel systems with liquid electrolytes. Electrochemical and rheological testing is underway. Cathode areas of up to 12 cm^2 have been prepared in the glove box and will be compared with cathodes prepared using the BATT program cell development equipment for comparison. Progress towards Milestones 1 and 3 is satisfactory as a result of these activities.

- **Further plans to meet or exceed milestones**. Experiments with highly purified PEO are underway to examine the effect of additives on polymer electrolyte stability and behavior. It has already been noted that the very pure material is more liquid-like due to the removal of the filler present in all PEO samples available commercially.

TASK STATUS REPORT

PI, INSTITUTION: S.A. Khan, P.S. Fedkiw, North Carolina State University; G.L. Baker, Michigan State University

TASK TITLE - PROJECT: Electrolytes - Composite Polymer Electrolytes for Lithium and Lithium-Ion Batteries

SYSTEMS: Li/polymer

BARRIER: Short lithium battery lifetimes and high costs.

OBJECTIVES: The ultimate objectives are to develop composite polymer electrolytes that are low-cost, have high conductivities, impart electrode-electrolyte interfacial stability, and yield long cycle life.

APPROACH: Our approach is to use surface-functionalized fumed silica fillers in BATT-baseline systems to determine the effects of filler type and concentration on interfacial stability and cell cycling. We intend to correlate these electrochemical characteristics with mechanical properties and materials chemistry (*e.g.*, silica-type or PEO-type, synthesized by Baker or Kerr, respectively). Data to be collected include modulus, ionic conductivity, Li cycling efficiency, Li-electrolyte interfacial resistance, and full-cell cycling capacity using 3-V cathodes.

STATUS OCT. 1, 2001: We established that fumed silica-based composite electrolytes with low-molecular weight PEOs exhibit conductivities exceeding 10^{-3} S/cm at 25ºC and have electrochemical properties (Li transference number, conductivity) decoupled from mechanical properties, thus providing a range of mechanical modulus (as high as 10^5 Pa). We determined that fumed silica stabilizes the Li/electrolyte interface effectively suppresses Li dendrite growth, and significantly improves cycle performance and electrochemical efficiency. We also observed that different surface groups present on the silica effect varied improvement on electrochemical performance in both half- and full-cell studies with a V_6O_{13} cathode. Fumed silica A200 having 100% hydrophilic silanol surface groups exhibits better electrochemical performance than R805 having 48% hydrophobic octyl surface groups.

EXPECTED STATUS SEPT. 30, 2002: Using the baseline high-molecular weight PEO + LiTFSI system, we expect to determine the effect of fumed silica on conductivity and electrolyte/Li interfacial stability and how these results vary with type of fumed silica surface group.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES:

1. Develop protocols for incorporating varying amount of fumed silica with a variety of surface chemistries (*e.g.*, -OH, octyl-, and crosslinkable moieties) into LBNL baseline polymer electrolytes. (March 2002)
2. Complete Li/CPE/Li and full-cell cycling studies using 3-V vanadium oxide cathodes with composites developed from milestone 1. (September 2002)
3. Acquire rheological data for materials generated from milestone 1 for correlation with electrochemical stability. (September 2002)

PROGRESS TOWARD MILESTONES

Accomplishments toward milestone over last quarter:

We are using conductivity measurements as a tool to develop protocols for dispersing homogeneous fumed silica in base-line materials (Milestone 1). We have conductivity results for high-MW PEO (MW= 2×10^5 and 6×10^5) + LiTFSI + fumed silica systems: (1) In $P(EO)_{10}LiTFSI$ (O:Li=10) electrolyte, the conductivity at temperatures from 15 to 90°C decreases with addition of hydrophilic A200 or hydrophobic R805 fumed silica; (2) In the $(PEO)_{20}LiTFSI$ system, the conductivities increase at temperatures from 15 to 50°C with the addition of the fumed silica but decrease above 50°C . Adding nanoparticles of fumed silica improves the rheological properties of polymer electrolytes, whereas the addition of fillers can be either beneficial or detrimental to ion-transport behavior. In crystalline polymer electrolytes, adding fillers increases the conductivity as the crystallinity always decreases. In amorphous polymer electrolytes, adding fillers decreases conductivity due to a volume-dilution effect. This mechanism explains our conductivity results.

We have set up a new temperature-controlled system for Li/Li or full-cell cycling above ambient temperature (Milestone 2), and obtained some preliminary results. Li/CPE/Li cells were cycled at current density of 0.1 mA/cm^2 with fixed charged density 60 mC/cm^2. Three different electrolytes based on the high-MW PEO (MW= 6×10^5) were used to evaluate the interfacial stability: (1) $P(EO)_{20}LiTFSI$ (O:Li=20); (2) $P(EO)_{20}LiTFSI$ + 10 wt% A200; (3) and $P(EO)_{20}LiTFSI$ + 10 wt% R805. The cell voltage oscillates for the electrolyte without fumed silica; whereas the cell voltage was more stable with fumed silica, which is similar to the behavior observed in the low-MW PEG-dM system. Adding fumed silica improves the interfacial stability of Li/composite polymer electrolyte. Further investigations continue.

We also have set up a new rheometer to acquire rheological data for high-MW PEO (Milestone 3). We have measured the dynamic rheology at 80°C of high-molecular weight (MW=2×10^5) PEO samples containing 0, 5, and 10 wt% A200, R805, and R974. At this temperature, the neat PEO behaves like a classic viscoelastic polymer with both the elastic (G') and viscous (G'') moduli showing strong frequency dependence and crossing over at a frequency of 5 rad/s. At a fumed silica concentration of 10 wt%, the crossover frequency is no longer observed in the measured frequency range (0.01 rad/s to 100 rad/s); further the G' is larger than G'' and much less frequency-dependent. These results imply a sample with significantly long relaxation time and the onset of elastic-like behavior. Thus, the fumed silica forms a network structure and provides mechanical support even when the PEO matrix has melted. The surface chemistry of the fumed silica affects the rheology of the PEO as well. For systems containing A200 (hydrophilic) silica, the frequency dependence of G′ is less than those systems containing R805 and R974 (hydrophobic) silica. This same trend has also been observed in the oligomer PEG-dM; that is, the A200-containing system is more elastic-like of the three.

Further plans to meet or exceed milestone: We continue to study the interfacial stability using Li/CPE/Li cycling. We will design new cathode compositions and process conditions using 3-V vanadium oxide for full-cell cycling. We will also continue to acquire rheological data for correlation with electrochemical stability.

•**Reason for changes from original milestone:** N/A

TASK STATUS REPORT

PI, INSTITUTION: D. DesMarteau and S. Creager, Clemson University

TASK TITLE - PROJECT: Electrolytes - New Battery Electrolytes based on Oligomeric Lithium bis((perfluoroalkyl)sulfonyl)imide Salts

SYSTEMS: Li/polymer

BARRIER: Short Li battery lifetime. Low Li battery power density.

OBJECTIVES: (1) Develop methods for synthesizing oligomeric ionene Li salts based on the bis((perfluoroalkyl)-sulfonyl)imide anion. (2) Develop methods for preparing solid polymer electrolytes (SPEs) from the target salts. (3) Provide data on the ionic conductivity and Li transference of the target SPEs at variable temperature and composition. We expect these studies will lend insight into the effects of anion size, chain length, and linker structure on SPE ionic conductivity and Li transference.

APPROACH: Salts will be synthesized using methodologies developed at Clemson over the last 15 years (D. DesMarteau, *J. Fluorine Chem*. 1995, **72**, 203-208). SPEs will be prepared from crosslinked low-MW polyethylene glycol (PEG) and also non-crosslinked PEG for comparison. Conductivities will be measured using electrochemical impedance spectroscopy.

STATUS OCT. 1, 2001: Contract was signed to initiate project in late Jan. 2002.

EXPECTED STATUS SEPT. 30, 2002: Dimeric salts with different perfluorinated chains linking sulfonyl imide anion groups together, and oligomeric ionene salts utilizing the same linkers in longer chains, will have been synthesized. SPEs from the salts will have been fabricated in polyether matrices, and their ionic conductivities measured at various temperatures and compositions. A method for measuring Li^+ transference based on DC potentiostatic polarization is being implemented, and progress in measuring Li^+ transference in the target SPEs will have been made.

RELEVANT USABC GOALS: 10 year life, <20% capacity fade over 10 year period, 1000 cycles.

MILESTONE: Our two major project milestones are as follows:
1. Synthesize new ionene Li salts based on oligomeric bis((perfluoroalkyl)sulfonyl)imide anion structures.
2. Characterize the electrical properties of polyether-based solid polymer electrolytes from the target salts at variable temperature and salt content.

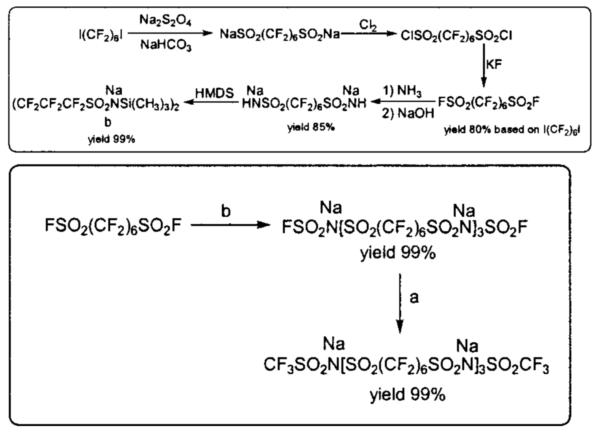
Progress toward the milestones will be ongoing as new salts are synthesized and are made available for characterization. Synthetic and characterization work on dimeric Li salts should be completed by Sept 30, 2002. Synthesis and characterization of oligomeric salts should be started and preliminary results obtained by Sept 30, 2002.

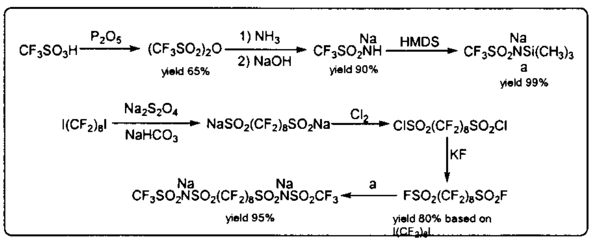
PROGRESS TOWARD MILESTONES

Accomplishments toward milestone over last quarter:

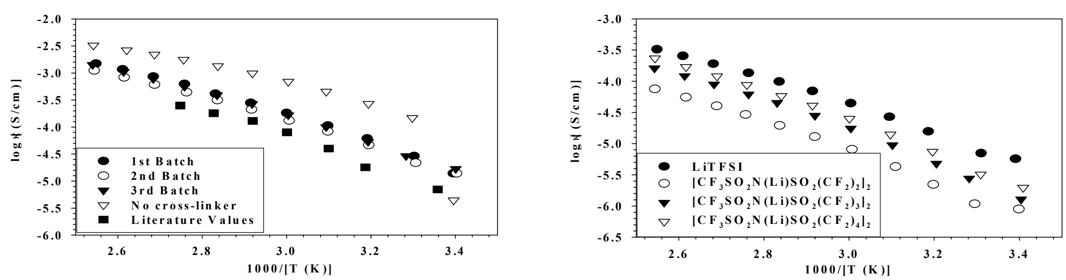
<u>Synthesis.</u> Synthesis of a series of dimeric salts of general structure $CF_3SO_2N(Li)[SO_2(CF_2)_nSO_2N(Li)]SO_2CF_3$ (n = 4, 6, 8) was completed and testing of SPEs from these salts is underway (see below). Scheme 1 presents a representative synthesis of a dimer with a perfluorooctyl chain between two imide anions. Scheme 2 presents a related synthesis of a tetra-anionic salt with perfluorohexyl chains linking imide anions. Excellent yields are obtained in all steps.

Scheme1 1, bottom, synthesis of a dilithium salt based on the imide anion. **Scheme 2**, right, synthesis of a tetra-anion salt.





<u>Characterization.</u> Solid polymer electrolytes based on low molecular weight PEG (M_w = 2,000) cross-linked with 4,4',4"- methylidyne-tris(phenylisocyanate) (Desmodur RE, M_w = 367 g/mol) were prepared using CF_3SO_3Li (LiTf), $(CF_3SO_2)_2NLi$ (LiTFSI), and dilithium salts based on anions of general structure shown above. Two trends are notable in the ionic conductivity in these SPEs. First, crosslinking the PEG matrix always diminishes ionic conductivity over the full temperature range (Figure 1, left). This diminished conductivity is compensated by an improved tractability and dimensional stability of the crosslinked materials, which justifies their use. Second, ionic conductivity in the series of dilithium-salt-based SPEs in crosslinked PEG exhibits the same trends as in non-crosslinked PEG, namely the salts with the largest dianion having the most perfluorination in the chain linking the two imide anions exhibit the highest conductivity, almost equal to that of the monomeric salt LiTFSI. This trend is thought to reflect a diminished basicity of the more perfluorinated anions which helps to suppress ion pairing and increase the number of free ions in the SPE. A finding of high ionic conductivity in a dilithium-salt-based SPE is promising since Li transference is expected to be greater in SPEs from dimeric Li salts than in those from monomeric salts.



Arrhenius plots of ionic conductivity for lithium SPEs. Left, comparison of three separate preparati of cross-linked PEG and one of non-crosslinked PEG with LiTFSI (EO/Li = 18/1). Right, SPEs fro cross-linked PEG and three different dimeric lithium salts (EO/Li = 30/1).

TASK STATUS REPORT

PI, INSTITUTION: G.D. Smith, University of Utah

TASK TITLE - PROJECT: Electrolytes - A Molecular Dynamics Simulation Study of the Influence of Polymer Structure on Complexation Thermodynamics, Kinetics and Transport of Lithium Cations in Polyether-based Solid Polymer Electrolytes

SYSTEMS: Li/polymer

BARRIER: Low ionic conductivity of the polymer electrolytes. Low Li battery power density.

OBJECTIVES: The primary objective is to understand influence of polymer structure on thermodynamics, kinetics and Li-ion transport in polymer electrolytes.

APPROACH: Our approach is to perform molecular dynamics simulations of poly(ethylene oxide), poly(oxymethylene oxide), poly(oxytrimethylene), and poly(propylene oxide) doped with $LiBF_4$ salt in order to understand the influence of polymer structure on thermodynamics, kinetics and Li-ion transport in polymer electrolytes. Force fields for interactions of Li^+/BF_4^- with poly(ethylene oxide), poly(oxymethylene), poly(propylene oxide) are based on high-level quantum chemistry calculations of model compounds.

STATUS OCT. 1, 2001: The project was initiated on January 15, 2002.

EXPECTED STATUS SEPT. 30, 2002: Force fields for interaction of poly(ethylene oxide), poly(methylene oxide), poly(propylene oxide) with $LiBF_4$ will be developed. Molecular dynamics simulations of poly(ethylene oxide)/$LiBF_4$ and poly(oxymethylene)/$LiBF_4$ will be carried out yielding structural properties of these polymer electrolytes, ion self-diffusion coefficients, conductivities, and transport numbers. Changes in the Li^+ transport mechanism will be correlated with changes in polymer structure.

RELEVANT USABC GOALS: 10 year life, <20% capacity fade over 10 year period, 1000 cycles.

MILESTONE:

a) 05/01/2002. Perform MD simulations of poly(ethylene oxide)/$LiBF_4$ using the developed potential, which includes many-body polarization effects. Validate developed potential by comparing conductivity, structure, and polymer dynamics with the available experimental data.
b) 09/01/2002. Develop potential energy functions for poly(oxymethylene), poly(oxytrimethylene), poly(propylene oxide) with Li^+ and BF_4^-. Perform conventional equilibrium MD simulations of poly(oxymethylene), poly(oxytrimethylene), and poly(propylene oxide) with Li^+ and BF_4^-. Study the effect of polymer dynamics and the strength of polymer-Li^+ interactions on ion transport.
c) 09/30/2002. Perform free energy calculations of Li^+ salvation in poly(ethylene oxide), poly(oxymethylene). Correlate free energies with polymer electrolyte structures and Li-ion transport.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestones over last quarter:**

Quantum chemistry investigation of conformational energetics of dimethoxymethane and 1,3-dimethoxydimethylether (model compounds for poly(oxymethylene) and binding energetics of dimethoxymethane with Li^+ have been studied. Force fields for poly(methylene oxide)/Li^+ have been developed. MD simulations of poly(methylene oxide) oligomers have been initiated. MD simulations of poly(ethylene oxide)/$LiBF_4$ with various strengths of Li^+/polymer interactions have been initiated.

- **Further plans to meet or exceed milestones:** N/A

- **Reason for changes from original milestones:** N/A

TASK STATUS REPORT

PI, INSTITUTION: D.F. Shriver, S. Vaynman, Northwestern University

TASK TITLE - PROJECT: Electrolytes - Highly Conductive Polyelectrolyte-Containing Rigid Polymers

SYSTEMS: Li/polymer

BARRIER: Low ionic conductivity of the polymer electrolyte, electrochemical instability of the polymer electrolyte toward Li electrodes.

OBJECTIVES: The primary objective is to synthesize and test a new class of highly ionically conductive, rigid polymer electrolytes for rechargeable Li batteries.

APPROACH: Our approach is to modify the highly ion-conductive rigid polymer electrolytes previously synthesized at Northwestern University by replacing electrochemically unstable carboxy groups with more inert oxygen-rich functional groups such as sulfones, thus increasing the stability of the electrolyte toward Li electrode. At least two polymer-salt complexes will be synthesized, and their properties will be measured. These electrolytes will be tested in Li batteries.

STATUS OCT. 1, 2001: We synthesized highly conductive rigid polymer electrolytes that contain functional groups such as carboxy and sulfone and tested them in cells. Polymer-salt complexes that contain carboxy groups have high ionic conductivity (ca. 10^{-4} S/cm at room temperature), but are unstable toward Li. The ionic conductivity of three recently synthesized polysulfone-salt complexes is lower. One of the polymer electrolytes had ionic conductivity at room temperature approaching 10^{-4} S/cm. The stability toward Li of polymer-salt complexes that contain sulfone groups is much higher than that of polymer-salt complexes that contain carboxy groups.

EXPECTED STATUS SEPT. 30, 2002: This project will terminate on May 31, 2002. During the remaining four months we will synthesize promising polymer(s) in larger quantity, test their stability toward Li metal, and also test them in cells. We will prepare a final report that summarizes this research.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestones are:
1. To synthesize and test promising polymer systems by 4/2002 with the goal of conductivity higher than 10^{-4} S/cm at room temperature. The stability toward battery components should be high; the resistivity of the Li/polymer electrolyte cell should not increase more than a factor of two during the first week.
2. To prepare a final report by 5/31/2002.

PROGRESS TOWARD MILESTONES

A final report is being prepared.

TASK STATUS REPORT

PI, INSTITUTION: J. Kerr, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes - Electrolyte Additives

SYSTEMS: Low-cost Li-ion, high-power Li-ion

BARRIER: Safety of Li-ion batteries

OBJECTIVES: The primary objective is to identify chemical additives that improve the safety of nonaqueous electrolytes for Li-ion batteries by stabilizing the SEI layer on carbon.

APPROACH: The thermal stability of the ATD Program Gen 2 baseline electrolyte [1.2 M $LiPF_6$ in EC/EMC (3:7)] will be investigated by heating samples at 85˚C in sealed vials. Experiments will be conducted to determine the catalytic influence of cell components such as active electrode materials from the ATD Gen 2 chemistries on the thermal stability of the baseline electrolyte. Analytical techniques will be used to detect the presence of decomposition products from electrolytes in the presence of electrode materials. Capillary electrophoresis will be used to study Li salt degradation, and GC-MS will be used to study solvent degradation. Evidence suggests that the addition of an organic base such as pyridine reduces the decomposition rate of EC/DMC by limiting the disproportionation of $LiPF_6$. We plan to conduct further experiments with pyridine as an electrolyte additive. TEM and AFM will be used to study the effect of additives on the thickness and structure of the SEI layer and the irreversible capacity loss on carbon electrodes. Thermal analysis studies will be used to determine the thermal stability of carbon electrodes containing SEI layers.

STATUS OCT. 1, 2001: The polyether carbonates $(CH_2CH_2O)_mCOO)_n$ [PE_3C] were identified as possible decomposition products when 1 M $LiPF_6$ in 1:1 EC:DMC was heated to 85˚C. The PE_3C should simulate the end product that may be produced during the formation of the SEI layer (electrolyte decomposition) at the anode. The Illinois Institute of Technology (IIT) has evaluated PE_3C as an additive in 2016 coin cells (Li/carbon) containing 1 M $LiPF_6$-EC-DEC and the anode from ATD Program Gen 1 cells. Electrochemical studies showed that the presence of the electrolyte additive has a very small effect on the reversible capacity but produces a higher irreversible capacity loss. The negative electrodes from these coin cells were examined by TEM. There was no obvious difference in the SEI layer that was observed on graphite removed from cells with or without PE_3C additive. Pyrrole was investigated as an electrolyte additive. The irreversible capacity loss on graphite during the formation cycle was higher when pyrrole was present, suggesting it may have no benefit as an electrolyte additive.

EXPECTED STATUS SEPT. 30, 2002: We expect to complete studies on the catalytic effect of active electrode components on the thermal stability of the ATD Gen 2 baseline electrolyte. The study of pyridine in altering the thermal stability of the ATD Gen 2 baseline electrolyte will be completed

RELEVANT USABC GOALS: Identify additives that improve the safety of Li-ion batteries.

MILESTONES: Complete analysis of the thermal stability of 1.2 M $LiPF_6$ in EC/EMC (3:7) containing pyridine as an electrolyte (3/02).

PROGRESS TOWARD MILESTONES

Pyridine stabilizes the thermal reactions of this electrolyte in the bulk of the solutions. However, it is clear that there are reactions of the electrolyte with the electrodes that are complicated by the presence of the additive. These electrochemical reactions are still under study

The effect of addition of vinylene carbonate (VC) into LP40 electrolyte, 1M $LiPF_6$-EC-DEC(1:1 w/w).

The addition of additives such as vinylene carbonate has been found to greatly improve calendar and cycle life in Li ion batteries according to SAFT. It is generally thought that the reduction of the vinylene carbonate improves the behavior of the anode, and experiments have been initiated to investigate this.

A small amount (1~5 wt%) of vinylene carbonate (VC) was added into LP40 electrolyte. The cyclic voltammetry of ATD Program Gen 2 anode material was studied with scan rate of 0.5 mV/s. A reduction peak, perhaps VC, was observed between 2 and 2.5 V. This appears to result in lower Li intercalation performance at the carbon due to resistive film formation on to the carbon surface. Complete separation of the carbon film from the copper current collector and loss of adhesion of carbon particles were observed after long-term EIS tests in the presence of 5% VC. This results from an unknown reaction between VC or decomposition products and the PVDF binder used in the electrode.

In order to understand well the effect of VC, the concentration was reduced to 1~3 wt%. With increasing concentration of VC the intercalation current was decreased. EIS data were measured as a function of VC concentration. In case of 3 wt% VC, at less than about 2.5 V potential vs. Li interfacial impedances related to SEI formation were observed. This result is consistent with film formation due to reduction of the VC. The behavior of these films is under investigation.

TASK STATUS REPORT

PI, INSTITUTION: J. Prakash, Illinois Institute of Technology

TASK TITLE - PROJECT: Electrolytes - Nonflammable Electrolytes and Thermal Characterization

SYSTEMS: Li-ion cells

BARRIER: Thermal safety

OBJECTIVES: The goal of this proposal is to assist DOE/BATT in developing advanced high-performance Li-ion cells for electric and hybrid vehicles. The objectives of this project are: (1) to develop nonflammable electrolytes with high flash point (>100°C), ionic conductivity (10^{-3} S/cm), and wider voltage window (0-5 V *vs.* Li); and (2) to carry out thermal investigations of the flame-retardant (FR) additives in Li-ion cells.

APPROACH: Our research approach will include (1) the development of thermally stable and nonflammable electrolytes to provide safety and (2) thermal diagnostic studies of the Li-ion cells using differential scanning calorimetry (DSC) and accelerated rate calorimetry (ARC) in order to understand the degradation, failure, and safety mechanisms.

STATUS OCT. 1, 2001: We completed the synthesis of the FR hexa-methoxy-tri-aza-phosphazene N_3P_3 $[OCH_3]_6$ and supplied this material to ANL for further testing in PNGV Li-ion cells. We also completed the mechanistic studies of the interaction of the HMTAP with the anode in Li-ion cells and observed the existence of the Li-$P(OCH_3)_2$ species on the electrode surface.

EXPECTED STATUS SEPT. 30, 2002: This project is being discontinued and we expect to conclude the project by the end of September 2002. During this period, we will complete the electrochemical and thermal characterization of the FR additive HETAP in Li-ion cells using DSC and ARC. We will also complete the mechanistic studies of the FR additive HETAP in Li-ion cells in order to understand the catalytic reaction of the FR additive with the electrode/electrolyte during the requested extension of this project.

RELEVANT USABC GOALS: Thermal and fire safety of the EV batteries under normal and abusive conditions.

MILESTONES: The electrochemical, thermal, and mechanistic studies of the new flame retardant HETAP in Li-ion cells will be completed by the end of September 2002.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 over last quarter:**

1. Electrofuel Company (Canada) had shown considerable interest in our flame retardant HMTP and requested 7 grams of the material to test in their high capacity Li-ion cell. During this reporting period, we synthesized, characterized, and supplied about 7 grams of the HMTAP to the Electrofuel Company to evaluate its viability in high-capacity Li-ion cells.

2. Fig. 1 below shows the self-heat rate profile of the electrolyte with and without the HETAP additive in the ARC. It is evident that the maximum self-heat rate of the electrolyte without the flame-retardant additive is 0.68^{o}C/min, which occurs at T=177.6^{o}C. This can be attributed to the reaction of Li metal with the electrolyte. As the reaction proceeds, the Li metal is consumed, and thus the exothermic peaks decrease as the temperature increases beyond 177.6^{o}C. The HETAP in the electrolyte shows a broad exothermic peak starting at 182^{o}C with a maximum self-heat rate of 0.57^{o}C/min. In our earlier investigations, we have seen that the maximum self-heat rate of the electrolyte with the HMTAP flame-retardant additive was only 0.1957^{o}C/min at T=170.2^{o}C. This result shows that HETAP is inferior to HMTAP in terms of its thermal reduction properties.

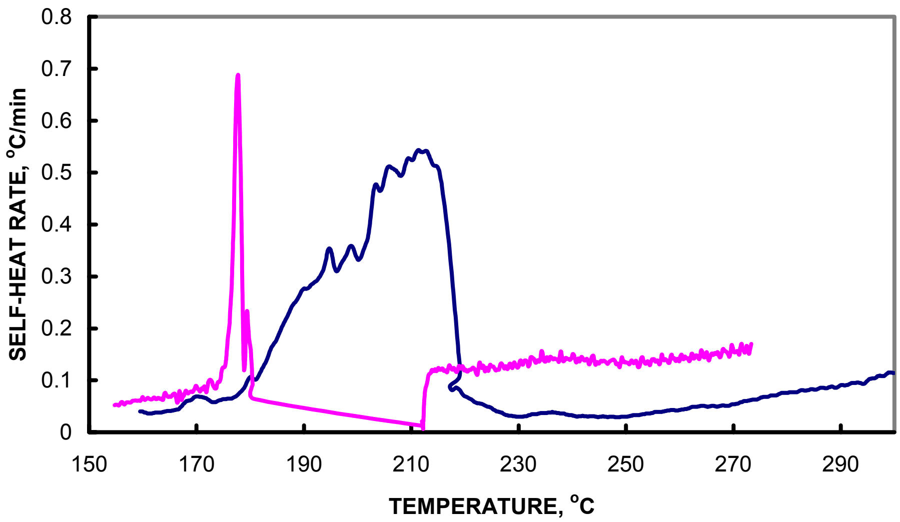


Figure 1. Thermal behavior of hexa-methoxy-tri-aza-phosphazene N_3P_3 $[OCH_3]_6$ in EC-DMC/1 M $LiPF_6$ electrolyte

3. We have also continued our spectroscopic studies (FT-IR, ^{1}H and ^{31}P NMR) on the electrodes (anode and cathode) removed from the Li-ion cells fabricated with the 5.0 wt% FR additive HMTAP. We will report he results of these studies in the next quarterly report.

- **Further plans to meet or exceed milestone:** Based on the ARC results on HETAP and our limited project time (September 2002 end date), we plan to terminate our studies on HETAP and focus on the mechanistic investigations on HMTAP in order to understand the catalytic reaction of the FR additive with the electrode/electrolyte especially at higher temperatures. We hope to complete the project by September 2002.

BATT TASK 4
CATHODES

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Cathodes - Novel Materials

SYSTEMS: Low-cost (Li-ion) battery and Li-polymer battery

BARRIER: Cost limitations of Li-ion and Li-polymer batteries

OBJECTIVES: To develop low-cost manganese-oxide cathodes to replace vanadium oxide electrodes in Li-polymer cells and cobalt electrodes in Li-ion cells.

APPROACH: Our approach is to search for, characterize, and develop low-cost manganese oxide electrodes that can be used in Li-ion and Li-polymer cells; the electrodes will be synthesized in the discharged and charged states, respectively. For Li-ion cells, focus will be placed on layered lithium-manganese oxide structures that do not convert to spinel during electrochemical cycling, particularly those stabilized by a Li_2MnO_3 component, and those with a $LiMn_{1-x}M_xO_2$ composition (M=Ni, Co); for Li-polymer cells. The electrode material of choice is stabilized α-MnO_2.

STATUS OCT. 1, 2001: We exploited the concept of using a Li_2MnO_3 component to stabilize layered $LiMO_2$ structures with the ultimate objective of stabilizing layered $LiMnO_2$. In particular, we expanded our synthesis efforts to include solid solutions of $xLi_2MnO_3 \bullet (1-x)LiMO_2$ compositions, where M = Mn, Ni, or Co, or a combination thereof. To date, these materials have yielded specific capacities of approximately 150 mAh/g between 4.5 and 3.0 V in Li half-cells at 50°C, but for less than 100 cycles. Studies of $xLi_2MnO_3 \bullet (1-x)LiMO_2$ compositions were initiated in which M′ = Ti, Zr, *i.e.*, with $Li_2M'O_3$ components that are isostructural with Li_2MnO_3.

EXPECTED STATUS SEPT. 30, 2002: Improvements in the electrochemical performance of $xLi_2MnO_3 \bullet (1-x)LiMO_2$ electrodes will have been achieved with a targeted goal of 160 mAh/g for 100 cycles at 50 °C in Li-ion cells. Layered $LiMn_{1-x}M_xO_2$ compounds (M=Ni, Co), in particular $LiMn_{0.5}Ni_{0.5}O_2$ that yield 150 mAh/g for 50 cycles at 50 °C in Li-ion cells will have been synthesized. Stabilized α-MnO_2 electrodes for Li-polymer cells will have been evaluated in collaboration with LBNL (J. Kerr); the targeted performance of these electrodes is 200 mAh/g for 100 cycles at 80°C. A detailed understanding of the structural/electrochemical property relationships in the above-mentioned electrode systems will have been gathered by a variety of techniques such as XRD, XANES, EXAFS, NMR, and HRTEM.

RELEVANT USABC GOALS: 10-year life, <20% fade over a 10-year period.

MILESTONES: (a) Synthesize and evaluate $LiMn_{1-x}M_xO_2$ compounds (M=Ni, Co) (April 2002); (b) achieve a technical target of 150 mAh/g for 50 cycles at 50 °C (June 2002); (c) achieve the targeted milestones for the performance of $xLi_2MnO_3 \bullet (1-x)LiMO_2$ electrodes in Li-ion cells and for stabilized α-MnO_2 electrodes in Li-polymer cells (September 2002).

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestones over last quarter:**

Extended galvanostatic cycling of $xLi_2M'O_3 \bullet (1-x)LiMn_{0.5}Ni_{0.5}O_2$ (M' = Ti or Zr, and x =0.03) composite electrodes at 50°C in Li cells were carried out (Fig. 1). The discharge capacity of $0.03Li_2TiO_3 \bullet 0.97LiMn_{0.5}Ni_{0.5}O_2$ at the 84^{th} cycle (50^{th} cycle at 50°C) was approximately 160 mAh/g and thus meets objective (b) in our milestones.

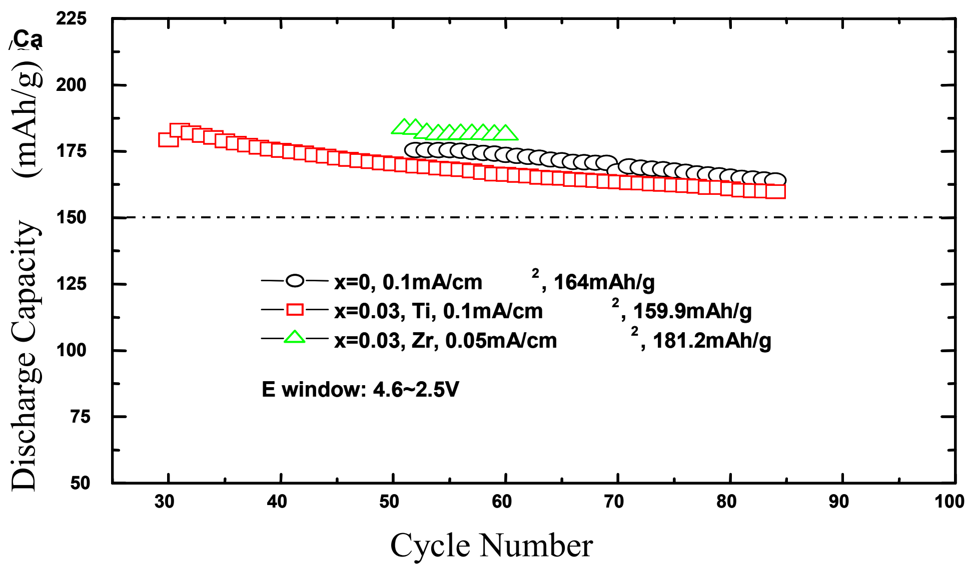


Figure 1. Galvanostatic cycling tests of Li/ $xLi_2M'O_3 \bullet (1-x)LiMn_{0.5}Ni_{0.5}O_2$ cells at 50°C. Note that the first 30 or 50 cycles of these cells, conducted at room temperature, are omitted for clarity.

In a new development, the electrochemical reactions of Li with layered composite electrodes $0.95LiMn_{0.5}Ni_{0.5}O_2 \bullet 0.05Li_2TiO_3$ (x=0.95) were investigated at low voltages. The metal oxide cathode, which can also be represented in layered notation as $Li(Mn_{0.46}Ni_{0.46}Ti_{0.05}Li_{0.02})O_2$, can react with one equivalent of Li during an initial discharge from 3.2 to 1.4 V vs. Li^0. The electrochemical reaction, which corresponds to a theoretical capacity of 286 mAh/g, forms $Li_2(Mn_{0.46}Ni_{0.46}Ti_{0.05}Li_{0.02})O_2$ that is isostructural with layered Li_2MnO_2 and Li_2NiO_2. This compound was also observed by XRD after chemical lithiation of $Li(Mn_{0.46}Ni_{0.46}Ti_{0.05}Li_{0.02})O_2$; the structure is hexagonally close-packed (space group *P-3m1*). Similar low-voltage electrochemical behavior was also observed with unsubstituted, standard $LiMn_{0.5}Ni_{0.5}O_2$ electrodes (x=1). *In situ* XAS data of $Li(Mn_{0.46}Ni_{0.46}Ti_{0.05}Li_{0.02})O_2$ electrodes suggests that the low-voltage (<1.8 V) reaction is associated primarily with the reduction of Mn^{4+} to Mn^{2+} to form $Li_2(Mn_{0.46}Ni_{0.46}Ti_{0.05}Li_{0.02})O_2$. The cycling behavior of $0.95LiMn_{0.5}Ni_{0.5}O_2 \bullet 0.05Li_2TiO_3$ electrodes over a large voltage window (4.6 to 1.1 V) was also studied. Preliminary results show that rechargeable capacities above 300 mAh/g can be obtained at C/20 rates. Future studies will concentrate on determining the optimal cycling conditions to balance capacity, coulombic efficiency and current rate.

- **Further plans to meet or exceed milestones:** We are focusing on meeting our goal of 160 mAh/g for 100 cycles at 50 °C by September 2002.

- **Reason for changes from original milestones:** N/A

TASK STATUS REPORT

PI, INSTITUTION: M.S. Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Cathodes – Novel Materials

SYSTEMS: Li/polymer/gel and low-cost Li-ion

BARRIER: Lower-cost, higher-capacity and safer cathodes

OBJECTIVES: The primary objective is to find lower-cost and higher-capacity cathodes, exceeding 200 Ah/kg, that are based on benign materials.

APPROACH: Our cathode approach is to place emphasis on manganese dioxides, both pure and modified with other transition metals, using predominantly low-temperature synthesis approaches. These materials will be synthesized and characterized, both structurally and for thermal and chemical stability. All will be evaluated electrochemically in a variety of cell configurations.

STATUS OCT. 1, 2001: We determined that layered manganese dioxides can be structurally stabilized, that their stability is a function of current density and/or cut-off voltages, that their electronic conductivity can be significantly enhanced, that their cell cycling can be substantially improved by addition of other transition metals, and that hydrothermally synthesized manganese oxides cycle as well as high-temperature materials. We also showed that vanadium oxides can also be stabilized by the addition of Mn ions, and that lithium iron phosphate can be synthesized very rapidly in a hydrothermal reactor.

- Layered $Li_xCo_yMn_{1-y}O_2$: ≥200 Ah/kg for 8 cycles, and stabilized Li_xMnO_2 ≥ 150 Ah/kg for 6 cycles
- Layered $Mn_{0.1}V_2O_5$; ≥ 200 Ah/kg for 6 cycles.

EXPECTED STATUS SEPT. 30, 2002: For low-cost Li-ion cells, we expect to identify the changes in $LiMnO_2$ structure as a function of current density in cell cycling, to determine the structure and composition of the vanadium-stabilized $LiMnO_2$ and to increase its electrochemical capacity. For Li/polymer cells we expect to complete the evaluation of the manganese-stabilized δ-vanadium oxides and to compare them to the iron phosphates. Emphasis in all cases will be placed on understanding the reasons for capacity fade. We will also have determined the feasibility of using a hydrothermal approach to the manufacture of lithium iron phosphate.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestones this year are: (a) to characterize the pillared manganese oxide, and improve its capacity to 150 mAh/g with an ultimate goal of 200 Ah/kg, (b) complete the characterization of manganese stabilized vanadium oxides and (c) to compare the best samples with iron phosphates for polymer or gel batteries by July 2002.

PROGRESS TOWARD MILESTONES

Accomplishments toward milestones over last quarter:

(a) Stabilized Manganese Oxide Cathodes

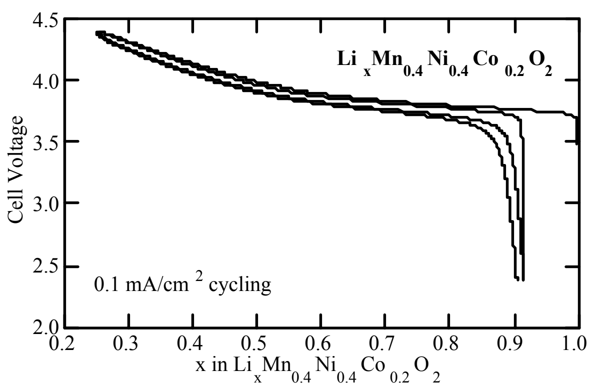
We are exploring the phase stability region of the vanadium-pillared layered manganese dioxides to find a material that has higher capacity at high discharge rates. A hollandite phase (2 x 2 tunnels) competes with the layer phase under most synthetic conditions and this phase reversibly cycles around 0.5 Li/Mn.

We continue to explore the impact of replacing some of the Mn by other transition metals. Earlier we showed that this doping by nickel, iron or cobalt enhances the electronic conductivity of the manganese oxide. This quarter we have explored the effect of the degree of replacement of Mn by Ni, whilst keeping some cobalt in the structure; in each case we kept the Li content at unity, $LiMMnO_2$. Three compounds were synthesized with formulae $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$, $LiMn_{0.3}Ni_{0.4}Co_{0.3}O_2$ and $LiMn_{0.4}Ni_{0.2}Co_{0.4}O_2$. These were cycled at 0.1 mA/cm^2 charge and discharge between 4.4 volts and 2.5 volts, and at 1 mA/cm^2 charge and 0.1 mA/cm^2 discharge between 4.6 and 2.5 volts. The first discharge capacity was related to the Ni content suggesting that the redox active specie is Ni which cycles between Ni^{2+} and Ni^{4+}. The charging regime for the cobalt is mostly above the 4.4 volt cut-off used here. The cycling behavior is shown below for one sample.

(b) Stabilized Vanadium Oxide and Iron Phosphate Cathodes

As noted last quarter we are emphasizing the iron phosphate formed at elevated temperatures as a comparison standard for our new cathode program. As also noted then the best performance is obtained for carbon loadings of 10 to 15 wt%, irrespective of whether the carbon is coated on during the synthesis and/or during the electrode preparation. We have now shown that loadings down to 6 wt% are effective though cell polarization is increased – see below. We met and compared data with LBNL researchers on $LiFePO_4$ this quarter, and will provide samples to LBNL for evaluation.

Our earlier data on $LiFe_{1-y}Mn_yPO_4$ was not particularly attractive, ≈ 0.5 Li cycling at steady state, but we have found that a wide range of other transition metals can be substituted for Fe in the iron phosphates and hydroxyphosphates.



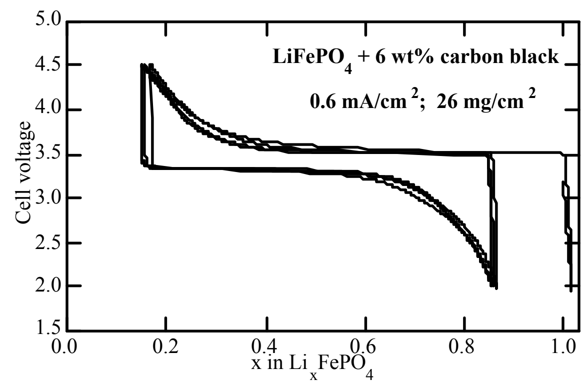


Figure 1. Cycling at room temperature of (left) $LiMn_{0.4}Ni_{0.4}Co_{0.2}O_2$ and (right) $LiFePO_4$ + 6 wt% carbon blacl at 0.6 mA/cm^2. [1 Li is 280 and 170 mAh/g for these compounds respectively].

- **Further plans to meet or exceed milestones:** N/A
- **Reason for changes from original milestones:** N/A

Publications: S. Yang, Y. Song, P.Y. Zavalij and M.S. Whittingham, "Reactivity, Stability and Electrochemical Behavior of Lithium Iron Phosphates," *Electrochem. Commun.*, **4** (2002) 239-234. (changed font size)
Y. Song, S. Yang, P. Y. Zavalij and M. S. Whittingham: Temperature-dependent properties of $FePO_4$ cathode materials, Mater. Res. Bull., 37 (2002) in press.

TASK STATUS REPORT

PI, INSTITUTION: M. Doeff, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cathodes - Synthesis and Characterization of Cathode Materials for Rechargeable Lithium and Lithium Ion Batteries

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Cost, cycle life, safety, and energy density

OBJECTIVES: To develop low-cost cathodes based on benign materials (*e.g.,* manganese oxides, lithium iron phosphates) having electrochemical characteristics (*e.g.*, cycle life, energy and power densities) consistent with the goals of the USABC and/or PNGV.

APPROACH: Cathode materials are synthesized using both conventional solid-state techniques and solution methods (*e.g.,* sol-gel, glycine-nitrate combustion). The microstructures and atomic structures of the materials are determined by relevant methods, and electrochemical analysis is carried out in a variety of cell configurations. Emphasis is placed on structurally stable materials such as tunnel-containing manganese oxides, as well as those of commercial interest, such as spinels and lithium iron phosphate.

STATUS OCT. 1, 2001: A milestone to provide $Li_{1.02}Al_{0.25}Mn_{1.75}O_{3.98}S_{0.02}$ to the BATT program in fall 2001 was met and samples of tunnel-containing Li_xMnO_2 were also provided. Several synthetic approaches for producing $LiFePO_4$ were evaluated, and sol-gel was considered the most promising.

EXPECTED STATUS SEPT. 30, 2002: Initial screening of novel P2 substituted layered manganese oxides will be completed, and a go/no go decision made based on the results. Recommendations will be made on the appropriateness of selected cathode materials for the BATT program. A design for an *in situ* x-ray diffraction cell will be finished.

RELEVANT USABC GOALS: 10-year life, < 20% capacity fade over a 10-year period.

MILESTONES:
1) Provide samples of conventional $LiFePO_4$ or sol-gel synthesized $Li_{1.02}Al_{0.25}Mn_{1.75}O_{3.97}S_{0.03}$ to the BATT program for testing (11/01): **completed**
2) Design *in situ* x-ray diffraction cell for structural studies of Li_xMnO_2 (6/02)
3) A Li/tunnel MnO_2 cell has been fabricated for an *in situ* XRD experiment at Sandia National Laboratory (Livermore, CA) using their cell holder design. Appropriate changes will be made to the design based on the outcome of the test.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

We will perform *in situ* XRD experiments with Dr. Gregory Roberts of Sandia National Laboratory (Livermore, CA), using their cell design and x-ray diffractometer, starting April 22nd. We hope to use the results from this to refine the cell holder design for eventual in-house experiments.

Li/1M $LiPF_6$, EC-DMC/O2-$Li_xM_{0.11}Mn_{0.89}O_2$ (M=Al, Fe, Ni) cells were assembled and tested. (Layered O2-$Li_xM_{0.11}Mn_{0.89}O_2$ materials were made by ion-exchanging P2-$Na_{0.7}M_{0.11}Mn_{0.89}O_2$ thoroughly). Lithium can either be extracted or inserted initially, depending upon the identity of M (Fig. 1). The initial charge for O2-$Li_xAl_{0.11}Mn_{0.89}O_2$ corresponds to about 140 mAh/g, competitive with manganese oxide spinels. In contrast to reports by Dahn *et al*., we see no evidence for irreversible phase conversions upon cycling for these materials. It is likely that incomplete exchange complicated earlier results, since replacement of Li for Na results in sliding of the MnO_2 layers. These structures are not expected to undergo conversion to spinel because the oxygen arrays are not cubic close packed as in R3_M layered materials.

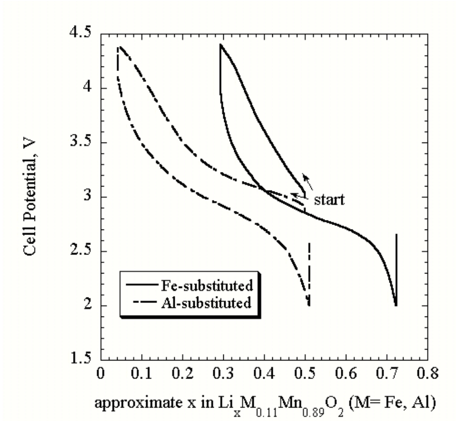


Figure 1. Initial charge and discharge of Li/1 M $LiPF_6$, EC-DMC/O2-$Li_xM_{0.11}Mn_{0.89}O_2$ (M=Al, Fe) cell at 0.05 mA/cm^2.

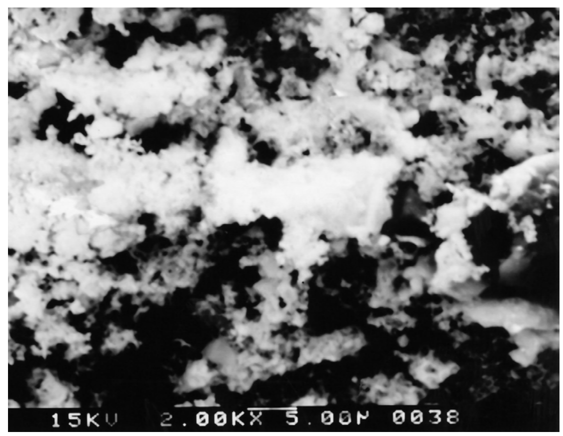


Figure 2. Scanning electron micrograph of $LiFePO_4$ prepared by a sol-gel technique.

A sol-gel process was used to prepare phase-pure $LiFePO_4$ from iron nitrate, lithium acetate, and phosphoric acid (Fig. 2). Electrodes made from this uncoated material delivered about half the theoretical capacity at low current densities, more than is generally obtained with uncoated $LiFePO_4$ made by conventional means. We believe this is due to the small particle size and flake morphology. More work is underway to improve the discharge characteristics of the sol-gel $LiFePO_4$.

- **Further plans to meet or exceed milestones** N/A
- **Reason for changes from original milestones** N/A

PUBLICATIONS

M.C. Tucker, M.M. Doeff, T.J. Richardson, R. Fiñones, J.A. Reimer and E.J. Cairns, "^{7}Li and ^{31}P MAS NMR of $LiFePO_4$-Type Materials", *Electrochem. and Solid State Letters*, **5**, A95 (2002). (changed font size)

TASK STATUS REPORT

PI, INSTITUTION: J. Evans and T. Devine, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Corrosion of Aluminum in Li Cell Electrolytes

SYSTEMS: High-power Li-ion battery

BARRIER: Limitations on cycle or “shelf” life.

OBJECTIVES: The primary objective is to quantify corrosion of aluminum when used in present or candidate Li cell electrolytes. Aluminum is a relatively inexpensive material that is widely used for the positive electrode current collector and cell containment.

APPROACH: The approach uses an electrochemical quartz crystal microbalance (EQCM) to determine the initial rates of corrosion of Al in BATT electrolytes as a function of potential and to discover whether passivation occurs. One of the Li salts ($Li(CF_3SO_2)_2N$) of the three baseline chemistries has been shown to corrode Al in prior LBNL work. Experiments on coated Al samples and longer term experiments (where exposed samples are examined at the scanning electron microscope) will also be conducted. As newer electrolytes (with higher performance characteristics or minimal CO_2 venting problems) are discovered their corrosivity to Al will be determined.

STATUS OCT. 1, 2001: No recent work on this project.

EXPECTED STATUS SEPT. 30, 2002: EQCM/cyclic voltammetry measurements completed on pure and carbon-coated Al samples in contact with three electrolytes most relevant to the BATT Program.

RELEVANT USABC GOALS: Cycle life >500 cycles.10-year life, <20% capacity fade over a 10-year period.

MILESTONE:
July 31: Measurements of the corrosion of Al in $LiPF_6$ + PC:EC:DMC(1:1:3) completed using the EQCM.
Sept. 30: Measurements of the corrosion of Al in $Li(CF_3SO_2)_2N$ + PEGDME (PEO analog) completed using the EQCM.

PROGRESS TOWARD MILESTONES

Person offered employment as postdoc. on this project declined position in favor of job in industry. Alternative candidate identified and process of hiring started. In the interim Dr. Seung-Wan Song of LBNL has joined the project part-time through July and is starting work on EQCM investigations on Al corrosion in $LiPF_6$ + PC:EC:DMC(1:1:3).

TASK STATUS REPORT

PI, INSTITUTION: J.B. Goodenough, University of Texas at Austin

TASK TITLE - PROJECT: Cathodes - Novel Materials

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Cost, cycle life, safety, and energy density

OBJECTIVES: To evaluate alternative layered oxides as cathode materials for a Li-ion battery that operates between Ni(II) and Ni(IV).

APPROACH: Layered $LiMO_2$ oxides have been shown to exhibit a high Li^+-ion mobility once a fraction of the Li is removed. On the other hand, these oxides are metastable and decompose on removal of a large fraction of Li from between the host MO_2 layers. $LiNi_{0.5}Mn_{0.5}O_2$ contains Mn(IV) and removal of Li operates on the Ni(III)/Ni(II) and Ni(IV)/Ni(III) couples, both of which are pinned at the top of the O^{2-}:$2p^6$ band. Ohzuku and Mikimura have demonstrated a capacity over the range 2.5 to 4.3 V *vs* Li that approaches 150 m Ah/g for 30 charge/discharge cycles at room temperature. We have found that the capacity decreases sharply at higher current densities, which we suspect is the result of poor conductivity. We will investigate (1) whether we can increase the capacity at higher current densities by coating the particles with carbon and (2) the role, if any, of the Mn(IV) ions. Since small particle sizes are probably necessary, sol-gel synthetic routes will be employed.

STATUS OCT. 1, 2001: New project initiated 4/2/02.

EXPECTED STATUS SEPT. 30, 2002: Preliminary data.

RELEVANT USABC GOALS: 10-year life, < 20% capacity fade over a 10-year period.

MILESTONES: (due in FY 2003)

Testing influence of carbon coating on layered and spine Ni^{2+}, Mn^{4+} compounds operating on Ni^{3+}/Ni^{2+} and Ni^{4+}/Ni^{3+} couples. Testing influence of ZnO as getter for HF in cells requiring $LiPF_6$ as the electrolyte.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter:** New project.

BATT TASK 5
DIAGNOSTICS

TASK STATUS REPORT

PI, INSTITUTION: F. McLarnon and R. Kostecki, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Electrode Surface Layers

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIER: Short lithium battery lifetimes

OBJECTIVE: Establish direct correlations between electrode surface changes, interfacial phenomena, and cell capacity/power decline.

APPROACH: Use ellipsometry, Raman spectroscopy, and advanced microscopic techniques to characterize electrodes taken from baseline BATT Program cells, as well as thin-film electrodes in model cells. Our goal is to identify changes in electrode surface morphology, electrode surface chemistry, and SEI thickness and composition, which accompany cell cycling.

STATUS OCT. 1, 2001: We identified changes in $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode surface chemistry which accompanied cycling in $LiPF_6$-EC-EMC electrolyte, and identified surface carbon loss as a potential cell degradation mode.

EXPECTED STATUS SEPT. 30, 2002: We expect to provide detailed characterization of surface processes (including changes in surface morphology, near-surface structure, chemistry, and SEI growth) on BATT Program $LiFePO_4$ cathodes and model thin-film $LiMn_2O_4$ cathodes.

RELEVANT USABC GOALS: 0 year life, < 20% capacity fade over a 10-year period.

MILESTONE: (a) Determine the effect of sulfur and Al additives on the structure, surface morphology and chemistry of $LiMn_2O_4$ electrodes (January 2002). (b) Characterize surface processes such as changes in surface morphology, chemistry, and SEI formation on $LiFePO_4$ and $Li_{1.02}Al_{0.25}Mn_{1.75}O_{3.97}S_{0.03}$ model thin-film cathodes (June 2002).

PROGRESS TOWARD MILESTONES

Accomplishments toward milestone (a) over last quarter: Completed (see previous BATT Program quarterly report, dated February 2002).

Accomplishments toward milestone (b) over last quarter: We continued *in situ* spectroscopic ellipsometry studies of thin-film $LiMn_2O_4$ spinel electrodes. Our objective was to determine how the electrode composition profile and structure change as the electrode is cycled at constant current in EC-DMC (1:1 by vol.) + 1M $LiPF_6$ electrolyte. This information will not only provide new insight into spinel electrode behavior, but also form the basis for further analysis of BATT Program cathodes. Figure 1 shows how the ellipsometer parameter Ψ varies with time (which is inversely proportional to the extent of Li intercalation in the spinel cathode) during the first charge half-cycle. Connecting the points at wavelength 4255 Å in these curves produces the upper curve in Fig.2, which includes five regions that correspond to five distinct regions of the accompanying potential-composition curve. We were able to accurately simulate the ellipsometric data in region I with a simple model, the one-dimensional growth of a linear Li-ion concentration gradient in the thin-film $LiMn_2O_4$ electrode. From our analysis we derived a Li^+-ion diffusion coefficient of 6.3×10^{-12} cm^2/s, a value which agrees well with published data, see *J. Electrochem. Soc.*, **145**, 3024 (1998). The change in slope of the Ψ-t curve in region II indicates that a phase transition took place. We were able to accurately simulate the ellipsometric data in region III with a complex double-gradient model, in which the electrode was assumed to contain two manganese oxide phases. From our analysis, we derived an apparent average Li^+-ion diffusion coefficient of 5.1×10^{-12} cm^2/s in this region. The positive Ψ-t curve slope in region IV implies that an additional phase transition took place as the cathode was further charged. We are now refining our theoretical analysis of these ellipsometric data and extending our work to cycled electrodes. We anticipate that the latter results will provide us with new information on the mechanism of electrode capacity fading. We are also preparing thin-film $LiFePO_4$ and $LiNi_{0.8}Co_{0.2}O_2$ cathodes for use in similar studies.

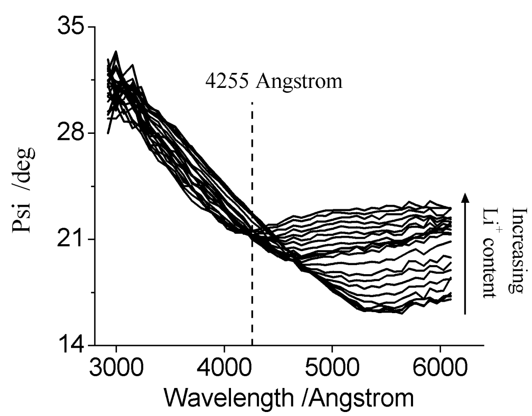


Figure 1. *In situ* spectroscopic ellipsometric curves for the first charge half-cycle in EC-DMC-$LiPF_6$ electrolyte.

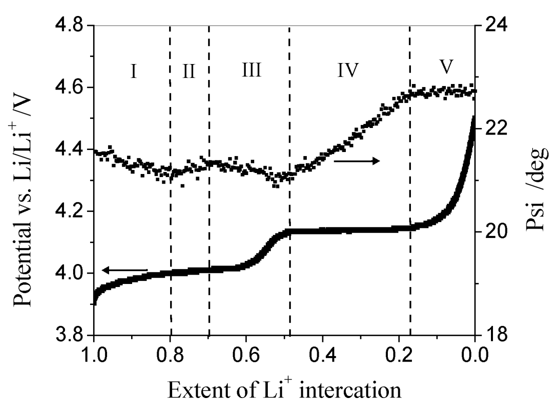


Figure 2. Charging curve for the first charge half-cycle (lower curve) and *in situ* spectroscopic ellipsometric curve at 4255 Angstrom (upper curve).

- **Further plans to meet or exceed milestone:** We anticipate a 3-month delay in the completion of our studies of model thin-film cathodes.
- **Reasons for changes from original milestone:** Certain components of the LBNL spectroscopic ellipsometer have degraded with age and become unreliable. Difficulties in identifying, correcting, and circumventing these problems have slowed our experimental efforts.

TASK STATUS REPORT

PI, INSTITUTION: J. McBreen Brookhaven National Laboratory

TASK TITLE - PROJECT: Diagnostics - Battery Materials: Structure and Characterization

SYSTEMS: High-power Li-ion, high-energy Li-ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective is to establish direct correlations between electrode materials changes, interfacial phenomena, and cell capacity decline.

APPROACH: Our approach is to use a combination of *in situ* and *ex situ* synchrotron techniques to characterize electrode materials and electrodes taken from baseline BATT Program cells. Techniques that are sensitive to both bulk and surface processes will be used. This will include both K and L-edge X-ray absorption spectroscopy (XAS) and transmission electron microscopy (TEM).

STATUS OCT. 1, 2001: We have completed an extensive study of the effect of Li and O stoichiometry on the phase behavior of spinel $LiMn_2O_4$ cathodes during cycling at ambient and at low temperatures. The effects of electrode history on the phase behavior of $LiMn_2O_4$ cathodes were also investigated.

EXPECTED STATUS SEPT. 30, 2002: We expect to complete our investigation of $LiMn_2O_4$ at 55°C. We also expect to complete our work on XAS at the P K-edge and its use in detection of electrolyte decomposition products. This will include application of the technique in the ATD Program. The cathode studies will include work on high capacity materials such as $LiFePO_4$ and substituted layered $LiMnO_2$.

RELEVANT USABC GOALS: 15-year life, <20% capacity fade over a 10-year period.

MILESTONES: (1) Complete stability studies of $LiMn_2O_4$ in LiF based electrolytes, at 55°C, by April 30, 2002. (2) Complete work on XAS at the P K-edge and apply it to materials from the ATD program by August 31, 2002. (3) Complete *in situ* XAS and XRD studies of $LiFePO_4$ and substituted layered $LiMnO_2$ by December 31, 2002.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 over last quarter:** We have completed our work on $LiMn_2O_4$ spinel cathodes. This work has included extensive electrochemical characterization, cycling studies, high-resolution *in situ* x-ray diffraction thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

The major findings and accomplishments of this milestone may be summarized as follows:

- *In situ* high resolution XRD has identified three phases during cycling on the 4.1 V plateau. This three-phase behavior is the inherent nature of the system. Before this work only two phases were observed. The existence of three phases with two first-order transitions explains the existence of two voltage plateaus during charge and discharge and two anodic and cathodic peaks in the cyclic voltammogram.

- The three-phase behavior can be clearly seen in stoichiometric $LiMn_2O_4$. In the case of stoichiometric $Li_{1-x}Mn_2O_4$ the onset of the second phase can be seen at x = 0.25. Recent work at Sony has confirmed that this is the spinel composition that has the lowest stability at elevated temperature (55°C). Increasing the Li stoichiometry between 1.0 and 1.1 increases the range of the lattice constants of all three phases. The result is pseudo-single-phase behavior upon cycling. This creates less strain on the lattice during cycling and improves cycle life. The excess Li stoichiometry also affects the electrochemical behavior on the 4.1 V plateau. It slightly decreases the capacity and results in sloping voltage plateaus. However, even with excess Li, a single potential excursion to the lower end of the 3 V plateau permanently reduces the range of the lattice constants and results in clear three-phase behavior on all subsequent cycling on the 4.1 V plateau. This is one of the reasons why excursions to the 3 V plateau decrease cycle life.
- It is well known that some of the cubic spinel transforms to the tetragonal phase in the vicinity of 0°C. Work on this program has shown that the degree of oxygen deficiency determines the temperature of the transition, the kinetics of the transformation and the amount that is converted to the tetragonal phase. All three parameters increase with increasing oxygen deficiency. With no oxygen deficiency the temperature of the transformation is below 0°C, the kinetics of the transformation are slow and a negligible amount is converted to the tetragonal phase. The oxygen stoichiometry is the most important parameter controlling the stability of the spinel.
- This work has also shown that the electrolyte has a profound effect on $LiMn_2O_4$ stability at elevated temperature. Replacement of the conventional $LiPF_6$ electrolyte with one based on LiF and an anion complexing agent greatly improves the high temperature stability of $LiMn_2O_4$ on cycling. The formation of PF_5, a strong Lewis acid promotes solvent decomposition and the formation of acidic groups in the electrolyte. This promotes the disproportionation of Mn(III) to Mn(IV) and soluble Mn(II), hence the capacity loss. Our work also shows that the addition of our anion complexing agents to conventional $LiPF_6$ based electrolytes improves cycling stability of $LiMn_2O_4$ at 55°C.
- $LiMn_2O_4$ has too low capacity on the 4.1 V plateau for consideration in electric vehicles. However, the three-dimensional tunnel structure of the spinel results in excellent kinetics. This and cost considerations make it attractive for hybrid electric vehicles (HEV). It should be possible to get stable operation in HEV by using excess Li stoichiometry, eliminating oxygen deficiency, and by operation at 50% state of charge (SOC) or higher. Further improvements can be expected by use of dopants, coatings and stable electrolytes.
- **Further plans to meet or exceed milestone:** Complete
- **Reason for changes from original milestones:** Because of the limited energy density no work was done on $Li_{1.02}Al_{.25}Mn_{1.75}O_{3.97}S_{0.03}$.

- **Accomplishments toward milestone 2 over last quarter:** No work was done on milestone (2) during the quarter.

- **Accomplishments toward milestone 3 over last quarter:** A paper has been prepared on the *in situ* XRD studies were done on a carbon coated Si anode material that was obtained from Prof. Yoshio of Saga University. Substituted layered $LiMnO_2$ was obtained from two sources. Extensive *in situ* XRD and x-ray absorption spectroscopy (XAS) was done on a Ni substituted $LiMnO_2$ material. Two samples of carbon-coated $LiFePO_4$ were obtained from HQ. Extensive *in situ* XRD and x-ray absorption spectroscopy (XAS) was done on one of the samples.

TASK STATUS REPORT

PI, INSTITUTION: P.N. Ross, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics – Interfacial and Reactivity Studies

SYSTEMS: Low-cost Li-ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective is to establish direct correlations between electrode surface changes, interfacial phenomena, and cell failure.

APPROACH: Our approach is to use Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) to study model electrode/electrolyte combinations, *e.g.*, using glassy carbon electrodes and BATT Program electrolytes, to provide the basis to interpret more-complex spectra recorded for ATD Program cell materials.

STATUS OCT. 1, 2001: Used Density Functional Theory (DFT) to calculated oxidation potentials of different Li-ion battery electrolytes and additives.

EXPECTED STATUS SEPT. 30, 2002: Together with other members of the project, establish thermal and electrochemical stability of different Li-ion battery electrolytes and additives as a function of the state of charge using ATD Program Gen 2 electrode materials.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

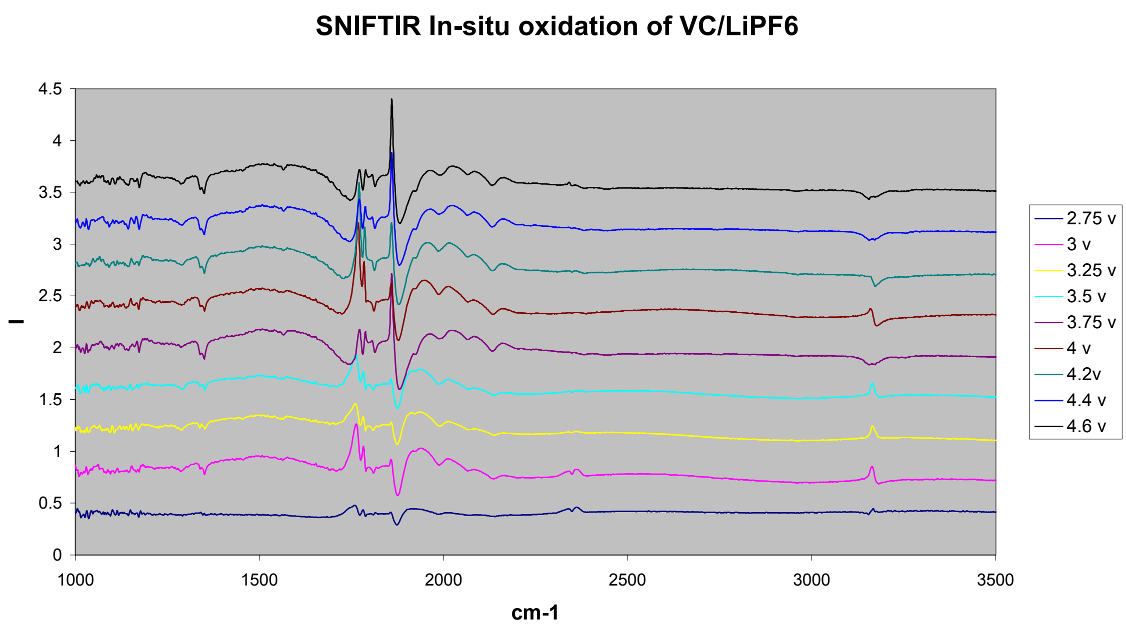
MILESTONES:
1. Determine onset potential for gas evolution from cathode materials as a function of composition of the electrolyte and the cathode material. (6/02)
2. Determine the kinetics of thermochemical reactions between the electrolyte and cathode materials as a function of temperature and composition. (9/02)

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 during last quarter:**

Vinylene carbonate (VC) has been proposed as an additive in PC electrolyte for Li-ion batteries. We have shown in both our previous computational and experimental studies that VC has a high reduction potential. Therefore it forms a passivation film on the carbon anode before the co-intercalation of PC molecule with Li+ into the anode. Our previous computational results, however, also indicated that VC would have a low oxidation potential (1 V lower than the saturated carbonates), which may not be a desirable feature for additives.

We have carried out some *in situ* electrochemical oxidation studies of electrolyte VC-$LiPF_6$. As mentioned in the last quarterly report, this IR cell has a CaF_2 window, a glassy carbon working electrode and Li metal as both counter and reference electrodes. The cell is assembled in the dry box. Subtractive normalized interfacial Fourier transform infrared (SNIFTIR) spectra show that a sharp peak at 1860 cm^{-1} starts to appear at potentials above 3.75 V. Not many functional groups have IR stretching in this region. The symmetric C=O stretching from a cyclic acid anhydride could produce such an IR feature. This observed oxidation potential of 3.75 V is very close to the calculated 4.06 V by the DFT calculations. It is also worthy of pointing out that the differences in calculated oxidation potential values between VC and ethylene carbonate (EC) are about the same as the differences in the experimental value between VC and EC, which is 1.5 V. Further studies would be carried out to investigate the oxidation mechanism of VC.



TASK STATUS REPORT

PI, INSTITUTION: E.J. Cairns, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Synthesis and Characterization of Electrodes

SYSTEMS: Li-ion and Li-polymer batteries

BARRIER: Rapid capacity fade

OBJECTIVES: The primary objectives are (1) to directly observe Li in BATT Program cathode materials, characterize the Li atomic and electronic local environment, and determine changes in this environment with cycling. Use this information to understand capacity fade, and to design new electrode materials.

APPROACH: Our approach is to use ^{7}Li MAS-NMR to characterize electrodes before and after cycling. Data to be collected are isotropic chemical shift, linewidth, and relaxation times for each species of Li. NMR data on model failure mechanisms will be used to interpret the spectra. Structural information and information on the local Li environment will be gathered to improve our ability to design new electrode materials.

STATUS, OCT. 1, 2001: We compared ^{7}Li MAS NMR spectra for stoichiometric and substituted tunnel-structure manganese oxides after electrochemical cycling. This information helps to elucidate the structural changes accompanying capacity fade. We initiated NMR analysis of fresh $LiFePO_4$-based materials, and began long-term cycling experiments on these materials.

EXPECTED STATUS SEPT. 30, 2002: We expect to have compared ^{7}Li MAS NMR spectra for a range of $Li(Mn,Fe)PO_4$ materials and Gen 2 electrodes at various states of charge. Cycled tunnel-structure materials will have been examined by MAS NMR for structural changes. The results will be helpful in interpretation of NMR spectra of cycled electrodes.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestones are to (1) Compare NMR-observable properties of baseline and novel electrodes, 9/02, (2) Measure capacities, capacity fading in our synthesized intermetallics, 6/02, (3) Use NMR to determine structural changes that cause capacity fade, 8/02.

PROGRESS TOWARDS MILESTONES

- **Accomplishments toward milestones during last quarter:**

^{7}Li MAS NMR spectra have been obtained for a variety of $LiFePO_4$-based materials and Gen 2 electrodes. We have determined the NMR shift and linebroadening mechanisms for $LiFePO_4$-based materials, thus securing the necessary information to provide sophisticated analysis of NMR spectra of mixed $Li(Mn,Fe)PO_4$ materials. We have obtained spectra of Gen 2 electrodes after various electrochemical tests. The results suggest that electrodes, which experience the greatest electrochemical degradation, tend to remain in a partially charged state at the end of discharge (and cell disassembly). This is probably due to SEI film formation during cycling. We are developing a NMR technique for quantifying the state of charge of an oxide electrode that is accurate to ~5%. This technique involves digesting 20 mg of the electrode in acidic solution, and using NMR to quantify the amount of Li extracted into the solution.

Using variable-temperature NMR, we have determined that the NMR shift mechanism for $LiFePO_4$-based materials is a hyperfine coupling of the ^{7}Li nucleus to unpaired Fe-site d electrons. Variable-field measurements suggest that the dominant linebroadening mechanism is chemical shift dispersion. This information will form the foundation for interpretation of NMR spectra of fresh and cycled $Li(Fe,Mn)PO_4$ materials.

NMR spectra of Gen 2 electrodes have been obtained after electrochemical cycling according to various protocols. Representative spectra are shown below.

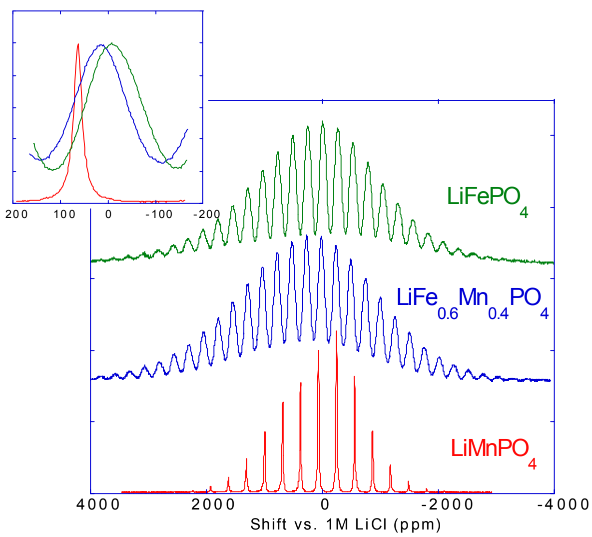


Figure 1. ^{7}Li MAS NMR spectra of representative olivine compositions

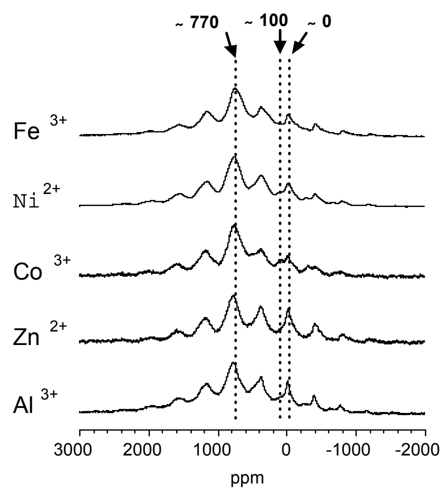


Figure 2. ^{7}Li MAS NMR spectra of $Li_y[M_{0.11}Mn_{0.89}]O_2$ with the layered O2-type structure

- **Further plans to meet or exceed milestones:**

- We will continue to analyze the NMR spectra using extended crystallographic structures to assign resonances.
- NMR spectra of the new O2-type lithium manganese oxides and $Li(MnFe)PO_4$ will be acquired at different states of charge and after repeated cycling, in order to follow the short range and long range changes in the structure, and to identify causes of capacity fade.

BATT TASK 6
MODELING

TASK STATUS REPORT

PI, INSTITUTION: J. Newman, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Modeling - Improved Electrochemical Models

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Poor polymer transport properties, side reactions, dendrite formation

OBJECTIVES: Develop experimental and computational methods for measuring and predicting transport, kinetic, and thermodynamic properties. Model electrochemical systems to optimize performance, identify limiting factors, and mitigate failure mechanisms.

APPROACH: Use galvanostatic polarization technique to measure a complete set of transport properties, which aids selection of improved polymer electrolytes. Develop molecular dynamics program to predict diffusion coefficients in multicomponent solutions. Use simulations and experiments to explore role of SEI layer in capacity fade in alloy and insertion electrodes. Develop model of factors affecting dendrite formation on Li metal. Use Raman spectroscopy to measure *in situ* concentration profile and dendrite growth.

STATUS OCT. 1, 2001: Measurements of the transport properties of PEMO-LiTFSI and refinement of both the galvanostatic polarization method and the transition-time verification method are completed. Modification of the molecular dynamics program to predict diffusion coefficients in multicomponent electrolytes, such as $LiPF_6$ in EC:PC, is ongoing. Measurements of the entropy of reaction in BATT baseline electrode materials are completed. Modeling of the SEI layer is ongoing. Diagnostic experiments of the SEI layer on lithium-tin electrodes are completed. Refinement of a model of dendrite growth to include mechanical stress and surface tension is ongoing, as is experimental work to observe dendrite growth and electrolyte concentration profiles using confocal Raman spectroscopy.

EXPECTED STATUS SEPT. 30, 2002: Analysis of the effect of side reactions on measurements of transport properties will be completed. Molecular dynamics simulations of diffusion coefficients will be completed. Modeling of the SEI layer will be ongoing. Inclusion of mechanical properties in the model of dendrite growth will be completed, and further refinements to the model will be ongoing. *In situ* confocal Raman spectroscopy measurements of dendrite growth and concentration profiles will be ongoing.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, <20% capacity fade.

MILESTONES:
1. Model of the effect of side reactions on transport property measurements. Completed.
2. Molecular dynamics simulation of $LiPF_6$ in carbonate solvents by Sept. 1, 2002.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 during last quarter:** Completed (see previous quarterly report).

- **Accomplishments toward milestone 2 during last quarter:** Diffusion coefficients have been calculated using the molecular dynamics simulation and are in qualitative agreement with experimental values for $LiPF_6$ in propylene carbonate and dimethyl carbonate/ethyl-methyl carbonate mixtures. We are currently implementing a tabulation procedure in the computer code which will speed up execution and allow more flexibility in the form of the intermolecular potentials used.

Other Progress

We have extended our understanding of heat effects from formation and relaxation of concentration gradients in electrochemical systems ("heat of mixing"), observable as the heat released while a cell is relaxing after interruption of the current. Previous work by Rao and Newman described how to calculate heat of mixing across a porous insertion electrode. We have extended this work to include heat of mixing within particles of insertion material and in the electrolyte. The magnitudes of the components of heat of mixing depend on the solid and salt diffusion coefficients, particle size, electrode thickness, partial molar enthalpy, and the current distribution. We have developed simple equations for estimating the magnitude of each component of heat of mixing.

We have extended the model of dendrite growth to account for mechanical forces in the separator and Li metal. Displacement and strain profiles for the cases of compressible and incompressible separators have been developed; both 2D and 3D cases have been examined. A separator material with a purely elastic response (no yielding) leads to yield of the ductile Li (prevention of dendrites) in all cases. However, real polymers exhibit viscoelastic behavior, depending on the degree of crosslink density. Since their behavior is more viscous than elastic, assuming a purely elastic response does not reflect the properties of attainable separator materials. Future work will expand the model to include viscoelastic polymer separators.

Refinements to the model of ion and electron transport through the SEI layer are ongoing.

In February 2002 a new post-doctoral researcher joined the group. Work has been initiated to model diffusion and reaction in the $LiFePO_4$ electrode, in order to quantify performance limitations. Work has also been initiated on understanding what happens when two dissimilar polymer-electrolyte separators are used in a cell. A possible method of achieving a high-voltage Li-polymer cell is to use two types of polymer electrolytes, one more stable to oxidizing potentials and the other more stable to reducing potentials. However, it is not clear as to what effect any difference in transport properties in the two polymers would have on the concentration/voltage behavior at the polymer-polymer interface. We have developed an analytic solution to the transport equations in this system, and will explore their implications in future work.

TASK STATUS REPORT

PI, INSTITUTION: A.M. Sastry**,** University of Michigan

TASK TITLE - PROJECT: Modeling - Failure Mechanisms in Li-ion Systems: Design of Materials for High Conductivity and Resistance to Delamination

SYSTEMS: Low-Cost Li-Ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective of these studies is to explain and predict the role of conductive and mechanical failures on reduced performance in the baseline systems, by tightly coupled experimental and simulation studies of microscale transport and mechanics phenomena.

APPROACH: Correlation of delamination, high impedance and temperature/structure/function phenomena with specific materials composition and morphology will be developed, making use of the extensive software developed for tracking mechanical and conductive losses in heterogeneous materials at UM. Specific comparisons will be undertaken, using cells provided by the ATD and BATT programs.

STATUS OCT. 1, 2000: We developed finite element representations of model carbon materials, and developed a means for measuring conductivity of thin electrodes.

EXPECTED STATUS SEPT. 30, 2001: We expect to confirm structure/function relationships in ATD Gen 1 and Gen 2 cells, through image analysis and testing, with verification from finite element simulations.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: We expect to test DOE ATD Program Gen 1 and 2 cells, provided by ANL, by May 31, 2002 (start date: 2/01).

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter:** We have completed some measurements on conductivity of materials provided by LBNL (Dr. Kathryn Striebel). We have also refined our analytical approach in interpreting experimental results from our four-probe experiment (Fig. 1). We have derived a closed-form approach which determines, independently, both contact resistivity and top-layer resistivity in electrodes. This analytic approach is an improvement to our previous model.

To summarize our efforts, we have continued work in three areas:

1. Experimental conductivity mapping of materials provided by three DOE-sponsored laboratories, has continued, using a sensitive four-probe conduction experiment.
2. We have obtained an analytical solution which elucidates tip and tip spacing effects, and have shown that our previous results were well within sensitive range for the experiment (for determination of top-layer resistivity). We have a newer approach which allows closed-form determination of contact resistivity.
3. Quantification (sensitivity analysis and numerical simulation) of expected experimental uncertainty, and comparison with experimental results has continued through refinement of the 2D solver for conductivity of particles, augmented by a newer set of findings in percolation of ellipses.

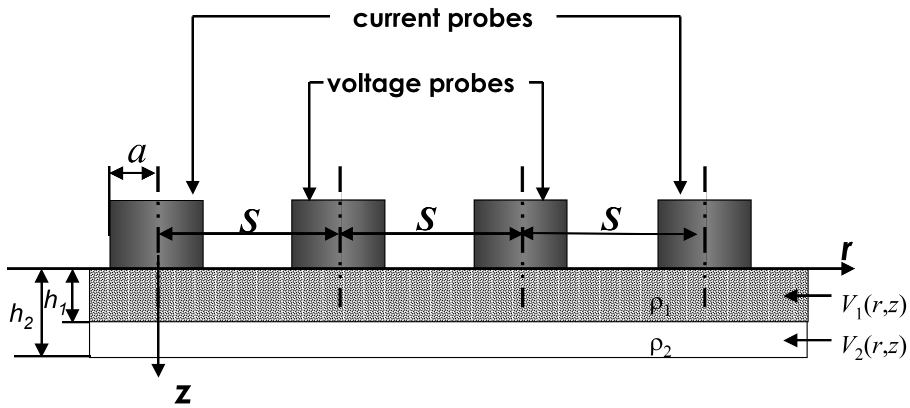


Figure 1. Schematic of four-probe conduction experiment.

From the LBNL materials, the anode electrodes of the four sets, i.e. low-cost baseline, GDR, SL-25, and Quallion anode, were tested; results are summarized in Table 1.

Table 1. Resistivities test results and their manufacture process of the four sets of anode electrode.

Electrode no.	Electrode Category	Electrode Name (LBNL)	Electrode Condition	Resistivity (μΩcm)	Stdev Resistivity (μΩcm)	contact resistance (μΩ cm^2)	Stdev contact resistance
028-09-4	Anode	SL20-4	unpressed	7.99E+05	2.39E+05	3.24E+05	8.60E+04
028-09-5	Anode	SL20-4	pressed	7.50E+05	2.28E+05	3.87E+05	9.38E+04
028-09-6	Anode	SL20-4	pressed	7.71E+05	1.11E+05	4.93E+05	4.45E+04
028-12-1	Anode	GDR14-1	unpressed	1.60E+04	2.40E+03	1.85E+02	9.60E+01
028-12-3	Anode	GDR14-1	pressed	1.18E+04	2.11E+04	1.05E+03	1.51E+03
028-12-4	Anode	GDR14-1	pressed	1.44E+04	2.35E+04	1.22E+03	1.51E+03
028-12-5	Anode	GDR6-1	unpressed	7.91E+04	1.49E+05	1.86E+04	4.48E+04
028-12-6	Anode	GDR6-1	pressed	1.49E+05	9.21E+04	1.69E+04	1.04E+04
028-12-7	Anode	GDR6-1	pressed	8.73E+04	4.86E+04	1.45E+04	4.20E+03
028-15-1	Anode	Quallion Electrode	unpressed	2.15E+05	8.90E+04	2.32E+04	6.52E+03

Table 2. Resistivities and composition of LBNL (NG7) and IREQ materials.

Material	Source	compositions				Resistivity (μΩcm)	Resistivity Stdev μΩcm	contact resistance (μΩcm2)	stdev contac resistance (μΩcm^2)
		natural graphi (v.f.%)	MCMB (v.f.%)	carbon fibe (v.f.%)	PVdF (v.f.%				
material 1	LBNL	23.36	-	-	4.11	6.16E+05	3.04E+05	6.64E+04	3.48E+04
material 2	LBNL	27.14	-	-	4.77	1.63E+05	5.74E+04	2.11E+04	7.25E+03
material 3	IREQ	-	21.5	4.59	6.34	2.58E+04	2.94E+03	4.37E+03	1.98E+03
material 4	IREQ	-	22.3	6.6	5.1	2.37E+04	2.85E+03	3.96E+03	1.41E+03
material 5	IREQ	-	-	33.09	5.81	3.39E+04	1.48E+04	6.05E+03	2.20E+03
material 6	IREQ	-	-	32.83	5.77	5.39E+04	3.55E+04	9.59E+03	6.75E+03

Comparisons with other LBNL and IREQ anodes (natural graphite and carbon materials) we obtained previously are shown in Table 2.

- **Further plans to meet or exceed milestone:** We are continuing to test LBNL materials, per continued discussions with Dr. Striebel and Dr. Frank McLarnon. Upon completion of testing of electrodes, we will be able to draw clear conclusions about conduction and composition, and manufacturing conditions, since we have now tested a range of materials. Reduction of data will be automated to accomplish this. The integral expression of the voltage distribution among and within layered electrodes poses a challenge in numerical solution, in that the integral is highly oscillatory (a product of a Bessel function and a sinusoid). We are exploring both restatement of the boundary value problem in order to obtain a different integral form for the solution, and also a faster numerical implementation of the solution. When we achieve a satisfactory solution technique, we will make it available to the other BATT research groups.

PROPOSALS UNDER REVIEW

ORGANIZATION *(Principal Investigator)*	TITLE	STATUS
University of Utah *(G.D. Smith)*	A Molecular Dynamics Simulation Study of the Influence of Polymer Structure on Complexation Thermodynamics, Kinetics and Transport of Li Cations in Polyether-Based SPEs	Request for Proposal - Contract Placed
University of Texas at Austin *(J.B. Goodenough)*	Cathodes - Novel Materials	Unsolicited - Contract In Negotiation
North Carolina State Univ. *(S.A. Khan)*	Composite Polymer Electrolytes for Use in Lithium and Lithium-Ion Batteries	Renewal - Contract Placed
University of Michigan *(G.A. Nazri, M.D. Curtis)*	Novel Composite Anodes for Li-Ion Batteries	Renewal Contract Placed
SUNY @ Binghamton *(M.S. Whittingham)*	Novel Anode Materials Novel Cathode Materials	Renewal - Contract Placed
Massachusetts Inst. of Tech. *(G. Ceder)* SUNY @ Stony Brook *(C. Grey)*	High Capacity, Stable Cathode Materials in Lithium and Lithium-Ion Batteries	Unsolicited - Contract In Negotiation

BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT)

QUARTERLY REPORT FOR JANUARY – MARCH 2002

CALENDAR OF UPCOMING EVENTS

<u>May 2002</u>

12 - 17	201st Electrochemical Society Meeting – Philadelphia, PA – ECS Centennial Meeting (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org)
19 - 24	8th International Symposium on Polymer Electrolytes –Santa Fe, NM (Rose Romero, ISPE8 Materials Science and Technology Division, Los Alamos National Laboratory, MS G754, P. O. Box 1663, Los Alamos, NM 87545, USA; http://www.lanl.gov/ispe8)

<u>June 2002</u>

23 – 28	11th International Conference on Lithium Batteries (IMLB-11) – Monterey CA (IMLB 11 Conference Secretariat, c/o The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; http://www.electrochem.org/meetings/011/imlb11.html)

<u>July 2002</u>

14 – 19	EESAT 2002 - International Ceramics Congress - Materials for Electrochemical, Chemical, Nuclear and Environmental Applications – Florence Italy (Dr. Nancy Clark, Sandia National Laboratories, P.O. Box 5800, MS 0613, Albuquerque NM 87185; nhclark@sandia.gov; http://www.dinamica.it/cimtec)

<u>September 2002</u>

3 - 8	53rd ISE – Dusseldorf, Germany (Prof. J.W. Schultze, Institut fur Physikalische Chemie II, Universitat Dusseldorf, Universitatsstr 1, D-4000 Dusseldorf 1, Germany; fax: 49 2118112803; schultzj@rz.uni-duesseldorf.de)

<u>October 2002</u>

15 - 18	17th International Electric Vehicle Symposium & Exposition – Montreal, Canada (Ms. Pam Turner, EVS-17 Symposium Manager; (650) 365-2802; fax: (650) 365-2687; electricevent17@aol.com).
6 - 11	202nd Electrochemical Society Meeting – Salt Lake City, UT (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org)

<u>June 2003</u>

1 - 6	1st International Conference on Polymer Batteries and Fuel Cells (PBFC-1) – Jeju Island, Korea (PBFC-1 Conference Chairman, Department of Chemical and Biomolecular Engineering, KAIST, 373-1, Guseong-dong, Yuseong-gu, Daejon, 305-701, KOREA; http://pbfc.kaise.ac.kr)
22 - 27	4th Iinternational Solid State Ionics Meeting - Monterey, CA (Turgut Gur, Stanford University, turgut@stanford.edu), Asilomar

<u>August 2003</u>

31 – Sept. 5	54th ISE – Florianopolis, Brazil (Prof. L.A. Avaca)

<u>September 2004</u>

	55th ISE – Thessaloniki, Greece (Prof. E. Theodoridou)